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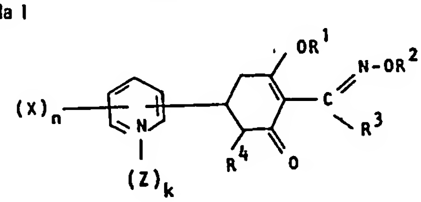
(54) Herbicidal cyclohexane-1,3-dione derivatives.

(57) The invention concerns novel compounds of the formula I



I

wherein:
Z is selected from oxygen and the group −YAn wherein Y is selected from C_1 to C_6 alkyl and benzyl and An is an anion;
k is zero or the integer 1;
n is zero or an integer selected from 1 to 4;
X is selected from halogen, nitro, cyano, alkyl, substituted alkyl, hydroxy, alkoxy, substituted alkoxy, alkenyl, alkenyloxy, alkynyl, alkynyloxy, acyloxy, alkoxycarbonyl, alkylthio, alkylsulfinyl, alkylsulfonyl, sulfamoyl, substituted sulfamoyl, alkanoyloxy, benzyloxy, substituted benzyloxy, amino, substituted amino and the groups formyl and alkanoyl and the oxime, imine and Schiff base derivatives thereof;
R^1 is selected from hydrogen, alkyl, alkenyl, alkynyl, substituted alkyl, alkylsulfonyl, arylsulfonyl, acyl and an inorganic or organic cation;
R^2 is selected from alkyl, substituted alkyl, alkenyl, haloalkenyl, alkynyl and haloalkynyl;
R^3 is selected from alkyl, fluoroalkyl, alkenyl, alkynyl, and phenyl; and
R^4 is selected from hydrogen, halogen, alkyl, cyano and alkoxycarbonyl.

The compounds of the invention show herbicidal properties and plant growth regulating properties and in further embodiments the invention provides processes for the preparation of compounds of formula I, intermediates useful in the preparation of the compounds of formula I, compositions containing as active ingredient a compound of formula I, and herbicidal and plant growth regulating processes utilizing compounds of formula I.

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Z/PP. 32870/EP

Herbicidal Cyclohexane-1,3-dione Derivatives

This invention relates to organic compounds having biological activity and in particular to organic compounds having herbicidal properties and plant growth regulating properties, to processes for the preparation of such compounds, to intermediates useful in the preparation of such compounds and to herbicidal compositions and processes utilizing such compounds and to plant growth regulating compositions and processes utilizing such compounds.

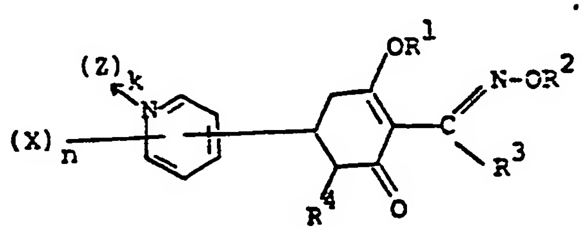
The use of certain cyclohexane-1,3-dione derivatives as grass herbicides is known in the art. For example, the "Pesticide Manual" (C R Worthing Editor, The British Crop Protection Council, 6th Edition 1979) describes the cyclohexane-1,3-dione derivative known commercially as alloxydim-sodium (methyl 3-[1-(allyloxyimino)butyl]-4-hydroxy-6,6-dimethyl-2-oxocyclohex-3-ene carboxylate) and its use as a grass herbicide. This compound is disclosed in Australian Patent No 464 655 and its equivalents such as UK Patent No 1 461 170 and US Patent No 3 950 420.

More recently, at the 1980 British Crop

Protection Conference ("1980 British Crop Protection Conference - Weeds, Proceedings Vol 1, Research Reports", pp 39 to 46, British Crop Protection Council, 1980), a new cyclohexane-1,3-dione grass herbicide code named NP 55 (2-N-ethoxybutrimidoyl)-5-(2-ethylthiopropyl)-3-hydroxy-2-cyclohexen-1-one) was announced. This compound is disclosed in Australian Patent No 503 917 and its equivalents.

It has now been found that a new group of cyclohexane-1,3-dione derivatives which have a 5-pyridyl substituent exhibit particularly useful herbicidal activity.

Accordingly the invention provides a compound of formula I or an isomer thereof



I

wherein:

Z is selected from oxygen and the group -YAn wherein Y is selected from C_1 to C_6 alkyl and benzyl and An is an anion selected from halide, tetrafluoroborate, methosulfate and fluorosulfate;

k is zero or 1;

n is zero or an integer selected from 1 to 4;

X, which may be the same or different, are independently selected from the group consisting of: halogen; nitro; cyano; C_1 to C_6 alkyl; C_1 to C_6 alkyl substituted with a substituent selected from the group consisting of halogen, nitro, hydroxy, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; hydroxy; C_1 to C_6 alkoxy; C_1 to C_6 alkoxy substituted with a substituent selected from halogen and C_1 to C_6 alkoxy; C_2 to C_6 alkenyloxy; C_2 to C_6 alkynyloxy; C_2 to C_6 alkanoyloxy; (C_1 to C_6 alkoxy)carbonyl; C_1 to C_6 alkylthio; C_1 to C_6 alkylsulfinyl; C_1 to C_6 alkylsulfonyl; sulfamoyl; N-(C_1 to C_6 alkyl)sulfamoyl; N,N-di(C_1 to C_6 alkyl)-sulfamoyl; benzyloxy; substituted benzyloxy wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, C_1 to C_6 alkyl, C_1 to C_6 alkoxy and C_1 to C_6 haloalkyl; the group NR^5R^6 wherein R^5 and R^6 are independently selected from the group consisting of hydrogen, C_1 to C_6 alkyl, C_2 to C_6 alkanoyl, benzoyl and benzyl; the groups formyl and C_2 to C_6 alkanoyl and the oxime, imine and Schiff base derivatives thereof;

R^1 is selected from the group consisting of: hydrogen; C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_1 to C_6 (alkyl) sulfonyl; benzenesulfonyl; substituted benzenesulfonyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to

C_6 alkoxy and C_1 to C_6 alkylthio; an acyl group; and an inorganic or organic cation;

R^2 is selected from the group consisting of: C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 haloalkenyl; C_2 to C_6 alkynyl; C_2 to C_6 haloalkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of halogen, C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio;

R^3 is selected from the group consisting of: C_1 to C_6 alkyl; C_1 to C_6 fluoroalkyl; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; and phenyl; and

R^4 is selected from the group consisting of: hydrogen; halogen; cyano; C_1 to C_6 alkyl; and (C_1 to C_6 alkoxy)-carbonyl.

When in the compound of formula I X is chosen from the groups formyl and C_2 to C_6 alkanoyl and the oxime, imine and Schiff base derivatives thereof, the nature of the oxime, imine and Schiff base derivatives is not narrowly critical. Although not intending to be bound by theory, it is believed that in the plant the (substituted) imine group may be removed to give the corresponding compound of formula I in which X is formyl or C_2 to C_6 alkanoyl. Suitable values for the groups formyl and C_2 to C_6 alkanoyl and the oxime, imine and Schiff base derivatives thereof include groups of the formula $-C(R^7)=NR^8$ wherein R^7 is chosen from hydrogen and C_1 to C_5 alkyl, and R^8 is chosen from hydrogen, C_1 to C_6 alkyl, phenyl, benzyl, hydroxy, C_1 to C_6 alkoxy,

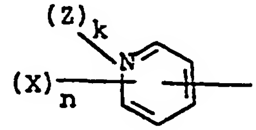
phenoxy and benzyloxy.

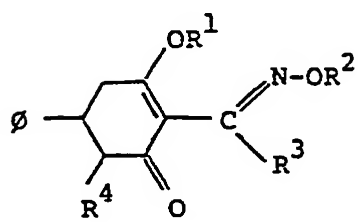
When in the compound of formula I R^1 is chosen from acyl the nature of the acyl group is not narrowly critical. Although not intending to be bound by theory, it is believed that when R^1 is acyl the acyl group may be removed in the plant by hydrolysis to give the corresponding compound of formula I in which R^1 is hydrogen. Suitable acyl groups include: alkanoyl, for example C_2 to C_6 alkanoyl; aroyl, for example benzoyl and substituted benzoyl wherein the benzene ring is substituted with from one to three substituents chosen from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; and heteroaroyl, for example 2-furoyl, 3-furoyl, 2-thenoyl and 3-thenoyl.

When in the compound of formula I R^1 is chosen from an inorganic or organic cation the nature of the cation is not narrowly critical. Although not intending to be bound by theory, it is believed that when R^1 is a cation the cation may be removed in the plant to give a compound of formula I wherein R^1 is hydrogen. Suitable inorganic cations include the alkali and alkaline earth metal ions, heavy metal ions including the transition metal ions, and the ammonium ion. Suitable organic cations include the cation $R^9R^{10}R^{11}R^{12}N^{\oplus}$ wherein R^9, R^{10}, R^{11} and R^{12} are independently chosen from the group consisting of: hydrogen; C_1 to C_{10} alkyl; substituted C_1 to C_{10} alkyl wherein the alkyl group is substituted with a substituent chosen from the group consisting of hydroxy, halogen and C_1 to C_6 alkoxy; phenyl; benzyl; and the groups substituted phenyl and substituted benzyl wherein the benzene ring is substituted with from one to three substituents chosen from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6

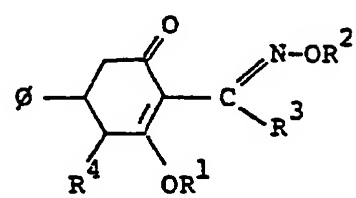
alkoxy and C_1 to C_6 alkylthio.

The compounds of the invention may exist in either of the two isomeric forms shown below or a mixture of these two isomeric forms, wherein Ø represents the group





Ia



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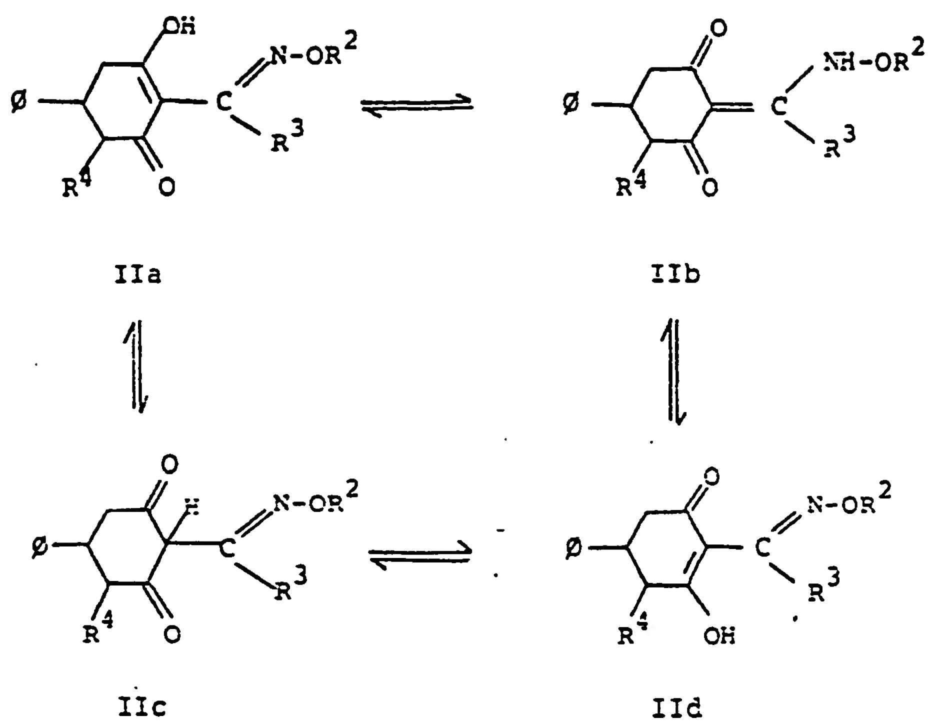
It should be recognized that when R^1 is hydrogen, the compounds of the invention may exist in any one, or in any mixture, of the four tautomeric forms shown below wherein Ø has the meaning defined above.



Suitable Z include oxygen.

Suitable k include zero or the integer 1.

Suitable n include zero and the integers 1 to 4.

Suitable X include: halogen; nitro; cyano; C_1 to C_6 alkyl; C_1 to C_6 alkyl substituted with halogen, nitro or C_1 to C_6 alkoxy; C_1 to C_6 alkoxy; C_1 to C_6 alkoxy substituted with halogen or C_1 to C_6 alkoxy; C_2 to C_6 alkanoyloxy; (C_1 to C_6 alkoxy)carbonyl; C_1 to C_6 alkylthio; C_1 to C_6 alkylsulfinyl; C_1 to C_6 alkyl-

sulfonyl; sulfamoyl; N-(C_1 to C_6 alkyl)sulfamoyl; N,N-di(C_1 to C_6 alkyl)sulfamoyl; benzyloxy; substituted benzyloxy wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, C_1 to C_6 alkyl, C_1 to C_6 alkoxy and C_1 to C_6 haloalkyl; the group NR^5R^6 wherein R^5 and R^6 are independently selected from hydrogen, C_1 to C_6 alkyl, C_2 to C_6 alkanoyl, benzoyl and benzyl; the groups formyl and C_2 to C_6 alkanoyl and the oxime, imine and Schiff base derivatives thereof.

Suitable R^1 include: hydrogen; C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_1 to C_6 (alkyl)sulfonyl; benzenesulfonyl; substituted benzenesulfonyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; an acyl group; and an inorganic or organic cation.

Suitable R^2 include: C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 haloalkenyl; C_2 to C_6 alkynyl; C_2 to C_6 haloalkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with substituent selected from the group consisting of halogen, C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6

haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio.

Suitable R^3 include: C_1 to C_6 alkyl; C_1 to C_6 fluoroalkyl; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; and phenyl.

Suitable R^4 include: hydrogen, halogen; cyano; C_1 to C_6 alkyl; and (C_1 to C_6 alkoxy)carbonyl.

Preferred compounds of the invention include those compounds of formula I wherein:

Z is the group -YAn wherein Y is selected from C_1 to C_6 alkyl and An is a halide anion;

k is zero or 1;

n is zero or an integer selected from 1 to 4;

X are independently selected from the group consisting of C_1 to C_6 alkyl, C_1 to C_6 alkoxy, C_1 to C_6 alkylthio; C_1 to C_6 alkylsulfinyl, C_1 to C_6 alkylsulfonyl, halogen and C_1 to C_6 haloalkyl;

R^1 is selected from the group consisting of: hydrogen; C_2 to C_6 alkanoyl; benzoyl and substituted benzoyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, C_1 to C_6 alkyl and C_1 to C_6 alkoxy; benzenesulfonyl and substituted benzenesulfonyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, C_1 to C_6 alkyl and C_1 to C_6 alkoxy; and an inorganic or an organic cation selected from the alkali metals such as lithium, potassium and sodium, the alkaline earth metals such as magnesium, calcium and barium, the transition metals such as manganese, copper, zinc, iron, nickel, cobalt and silver, the ammonium ion and the tri- and tetra-(alkyl)ammonium ions wherein alkyl is selected from C_1 to C_6 alkyl and

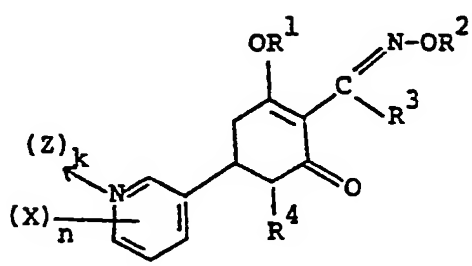
C_1 to C_6 hydroxyalkyl;

R^2 is selected from the group consisting of C_1 to C_6 alkyl, C_2 to C_6 alkenyl, C_2 to C_6 alkynyl, C_1 to C_6 haloalkyl, C_2 to C_6 haloalkenyl and C_2 to C_6 haloalkynyl;

R^3 is selected from C_1 to C_6 alkyl;

R^4 is selected from hydrogen, halogen and (C_1 to C_6 alkoxy)carbonyl.

More preferred compounds of the invention include those compounds of formula I in which the pyridine ring is linked through the 3-position to the cyclohexane ring and which have three or four substituents in the pyridine ring. That is, compounds of formula III:



III

wherein:

k is zero;

n is selected from the integers 3 and 4;

X are independently selected from the group consisting of C_1 to C_6 alkyl, C_1 to C_6 alkoxy, halogen and C_1 to C_6 haloalkyl;

R^1 is selected from the group consisting of hydrogen, C_2 to C_6 alkanoyl, benzoyl, the alkali metals, the transition metals, the ammonium ion and the tri- and tetra-(alkyl)ammonium ions wherein alkyl is selected from C_1 to C_6 alkyl and C_1 to C_6 hydroxyalkyl;

R^2 is selected from the group consisting of C_1 to C_3 alkyl, C_1 to C_3 haloalkyl, allyl, haloallyl and propargyl;

R^3 is selected from C_1 to C_3 alkyl; and

R^4 is selected from hydrogen and (C_1 to C_6 alkoxy)-carbonyl.

Even more preferred compounds of the invention include those 3-pyridyl compounds of formula III wherein:

k is zero;

n is selected from the integers 3 and 4;

X are independently selected from the group consisting of C_1 to C_6 alkyl, C_1 to C_6 alkoxy, halogen and C_1 to C_6 haloalkyl;

R^1 is selected from the group consisting of hydrogen, C_2 to C_6 alkanoyl and the alkali metals;

R^2 is selected from the group consisting of C_1 to C_3 alkyl, C_1 to C_3 haloalkyl, allyl, haloallyl and propargyl;

R^3 is selected from C_1 to C_3 alkyl; and

R^4 is hydrogen.

Particularly preferred values for X include

methyl, methoxy, ethoxy, bromo, chloro and trifluoromethyl.

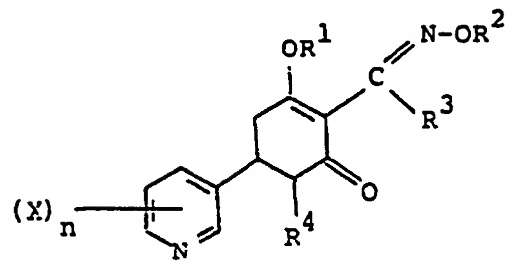
Particularly preferred values for R^1 include hydrogen, C_2 to C_6 alkanoyl, sodium and potassium.

Particularly preferred values for R^2 include ethyl, _n_-propyl, allyl, propargyl, fluoroethyl and chloroallyl.

Particularly preferred values for R^3 include ethyl and _n_-propyl.

Specific examples of the compounds of the invention include those compounds detailed in Tables 1a and 1b below

TABLE 1a



Compound No	$(X)_n$	R^1	R^2	R^3	R^4
1	all H	H	C_2H_5	$n-C_3H_7$	H
2	all H	H	a	$n-C_3H_7$	H
3	all H	H	b	$n-C_3H_7$	H
5	all H	H	C_2H_5	$n-C_3H_7$	c
6	$6-CH_3$	H	C_2H_5	$n-C_3H_7$	H
7	$2-Cl-6-CH_3$	H	C_2H_5	$n-C_3H_7$	H
8	$2-OCH_3-6-CH_3$	H	C_2H_5	$n-C_3H_7$	H
9	$2,4,6-(OCH_3)_3$	H	C_2H_5	$n-C_3H_7$	H
10	$2,6-Cl_2-4-CH_3$	H	C_2H_5	$n-C_3H_7$	H
11	$2,6-(OCH_3)_2-4-CH_3$	H	C_2H_5	$n-C_3H_7$	H
12	$2,4-Cl_2-6-CH_3$	H	C_2H_5	$n-C_3H_7$	H
13	$2-Cl-4-CF_3-6-CH_3$	H	C_2H_5	$n-C_3H_7$	H
14	$2-OCH_3-4-CF_3-6-CH_3$	H	C_2H_5	$n-C_3H_7$	H
15	$4-Cl-2,6-(CH_3)_2$	H	C_2H_5	$n-C_3H_7$	H
16	$2,6-Cl_2-4,5-(CH_3)_2$	H	C_2H_5	$n-C_3H_7$	H
17	$2-Cl-4,6-(CH_3)_2$	H	C_2H_5	$n-C_3H_7$	H

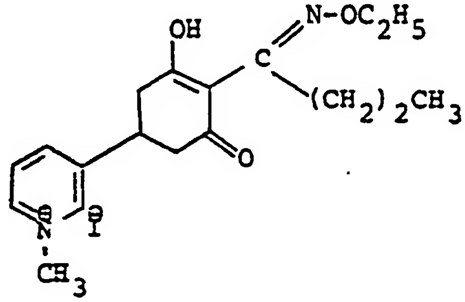
TABLE 1a - continued

Compound No	$(X)_n$	R^1	R^2	R^3	R^4
18	$2\text{-}OCH_3\text{-}4,6\text{-}(CH_3)_2$	H	C_2H_5	C_2H_5	H
19	$2\text{-}OCH_3\text{-}4,6\text{-}(CH_3)_2$	$Na^{\oplus}$	C_2H_5	C_2H_5	H
20	$2\text{-}OCH_3\text{-}4,6\text{-}(CH_3)_2$	H	C_2H_5	$n\text{-}C_3H_7$	H
21	$2\text{-}OC_2H_5\text{-}4,6\text{-}(CH_3)_2$	H	C_2H_5	$n\text{-}C_3H_7$	H
22	$2\text{-}SCH_3\text{-}4,6\text{-}(CH_3)_2$	H	C_2H_5	$n\text{-}C_3H_7$	H
23	$4,5\text{-}Cl_2\text{-}2,6\text{-}(CH_3)_2$	H	C_2H_5	$n\text{-}C_3H_7$	H
24	$2,5\text{-}Cl_2\text{-}4,6\text{-}(CH_3)_2$	H	C_2H_5	C_2H_5	H
25	$2,5\text{-}Cl_2\text{-}4,6\text{-}(CH_3)_2$	H	C_2H_5	$n\text{-}C_3H_7$	H
26	$5\text{-}Br\text{-}2\text{-}Cl\text{-}4,6\text{-}(CH_3)_2$	H	C_2H_5	$n\text{-}C_3H_7$	H
27	$5\text{-}Cl\text{-}2\text{-}OCH_3\text{-}4,6\text{-}(CH_3)_2$	H	C_2H_5	$n\text{-}C_3H_7$	H
28	$5\text{-}Cl\text{-}2\text{-}OCH_3\text{-}4,6\text{-}(CH_3)_2$	$Na^{\oplus}$	C_2H_5	$n\text{-}C_3H_7$	H
29	$2,4,6\text{-}(CH_3)_3$	H	C_2H_5	$n\text{-}C_3H_7$	H
30	$2\text{-}Cl\text{-}4,5,6\text{-}(CH_3)_3$	H	C_2H_5	$n\text{-}C_3H_7$	H
31	$2\text{-}Cl\text{-}4,5,6\text{-}(CH_3)_3$	d	C_2H_5	$n\text{-}C_3H_7$	H
32	$2\text{-}OCH_3\text{-}4,5,6\text{-}(CH_3)_3$	H	C_2H_5	$n\text{-}C_3H_7$	H
33	$2\text{-}OCH_3\text{-}4,5,6\text{-}(CH_3)_3$	H	e	$n\text{-}C_3H_7$	H
34	$2\text{-}OCH_3\text{-}4,5,6\text{-}(CH_3)_3$	H	f	$n\text{-}C_3H_7$	H
35	$2\text{-}OCH_3\text{-}4,5,6\text{-}(CH_3)_3$	H	b	$n\text{-}C_3H_7$	H

Code:

a	$CH_2CH=CH_2$
b	$CH_2CH=CHCl$
c	$CO_2C_2H_5$
d	$COCH_2CH(CH_3)_2$
e	$CH_2C\equiv CH$
f	CH_2CH_2F

TABLE 1b

Compound No	Structure
4	

The compounds of the invention may be prepared by a variety of methods and in a further aspect the invention provides methods for the preparation of compounds of formula I.

Conveniently the preparation of the compounds of the invention can be considered in three or four parts.

Part A involves the formation of a 5-arylcyclohexan-1,3-dione of formula IX. This reaction may be carried out in a two step process by:

(i) reacting, preferably in the presence of a base, an aldehyde derivative of formula V with acetone (IVa) or an acetone derivative of formula IVb to form a ketone derivative of formula VIa or VIb respectively; and reacting, preferably in the presence of a base, a ketone derivative of formula VIa with a malonic acid ester derivative of formula VIIa or a ketone derivative of formula VIb with a malonic acid ester of formula VIIb, to give an intermediate of formula VIIIa or VIIIb respectively which may be isolated or hydrolysed directly, preferably in the presence of an acid, to give a 5-arylcyclohexan-1,3-dione of formula IX, or reacting, preferably in the presence of a base, a ketone derivative of formula VIa with an alkanoic acid ester of formula VIIc to give a 5-arylcyclohexan-1,3-dione of formula IX;

(ii) reacting, preferably in the presence of a base, an aldehyde derivative of formula V with a malonic acid ester of formula VIIb to give an arylmethylidenemalonate derivative of formula VIc which is in turn reacted, preferably in the presence of a base, with an acetoacetic acid ester derivative of formula VIId to give an intermediate

of formula VIIIc which may be isolated or hydrolysed directly, preferably in the presence of an acid, to give a 5-arylcyclohexan-1,3-dione of formula IX; or

(iii) reacting, preferably in the presence of a base, an aldehyde derivative of formula V with an acetic acid ester of formula IVc to give a 2-arylalkenoate derivative of formula VId which is in turn reacted, preferably in the presence of a base, with an acetoacetic acid ester derivative of formula VIId to give an intermediate of formula VIIIa which may be isolated or hydrolysed directly, preferably in the presence of an acid, to give a 5-arylcyclohexan-1,3-dione of formula IX.

Part B involves the acylation of a compound of formula IX to give a 2-acyl-5-arylcyclohexan-1,3-dione of formula XIII. This reaction may be carried out by reacting a 5-arylcyclohexan-1,3-dione of formula IX with:

(iv) an acid anhydride of formula X in the presence of either an alkali metal salt of the corresponding acid of formula XI or an alkoxide salt of formula XII, wherein M is an alkali metal ion and R is C_1 to C_6 alkyl;

(v) an acid anhydride of formula X in the presence of the corresponding acid of formula XIV;

(vi) an acid halide of formula XV, wherein hal represents halogen, in the presence of a Lewis acid catalyst;

(vii) a mixture of an acid halide of formula XV and the

corresponding acid of formula XIV; or

(viii) with an alkali or alkaline earth metal hydride followed by reaction with an acid anhydride of formula X or an acid halide of formula XV.

Alternatively, this acylation reaction may be carried out by:

(ix) reacting a 5-arylcyclohexan-1,3-dione of formula IX with an acid halide of formula XV in the presence of pyridine to give an intermediate O-acyl derivative of formula XVI; and

(x) reacting the intermediate of formula XVI with a Lewis acid catalyst;

(xi) reacting the intermediate of formula XVI with the acid of formula XIV; or

(xii) reacting the intermediate of formula XVI with imidazole.

Part C involves the formation of a compound of the invention of formula I wherein R^1 is hydrogen, that is a compound of formula II. This reaction may be carried out either by reacting a 2-acyl-5-arylcyclohexan-1,3-dione of formula XIII with:

(xiii) an alkoxyamine derivative of formula XVII; or

(xiv) hydroxylamine to give an intermediate oxime derivative of formula XVIII and reacting that intermediate oxime derivative of formula XVIII with an alkylating agent of formula XIX wherein L is a leaving group such as, for example, chloride, bromide, iodide, sulfate, nitrate, methyl sulfate, ethyl sulfate, tetrafluoroborate,

hexafluorophosphate, hexafluoroantimonate, methanesulfonate, fluorosulfonate, fluoromethanesulfonate and trifluoromethanesulfonate.

Part D involves the formation of a compound of the invention of formula I wherein R^1 is a substituent other than hydrogen.

Compounds of the invention of formula I, wherein R^1 forms an ether, acyl or sulfonyl derivative of a compound of formula II, may be prepared from the corresponding compounds of the invention of formula II by reacting with an etherification, acylation or sulfonylation reagent of formula XX.

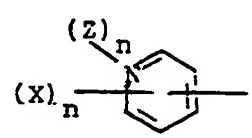
Compounds of the invention of formula I wherein R^1 is an inorganic or organic cation may be prepared from the compounds of the invention of formula I wherein R^1 is hydrogen, that is, compounds of formula II, by reacting said compounds of formula II with an inorganic or organic salt. For example, the compounds of formula I wherein R^1 is an alkali metal ion may be prepared by reacting the appropriate compound of formula II with the appropriate alkali metal hydroxide or alkoxylate. The compounds of formula I wherein R^1 is a transition metal ion or an organic cation may similarly be prepared by reacting the appropriate compound of formula II with an appropriate transition metal salt or organic base. Alternatively, the compounds of formula I wherein R^1 is a transistion metal ion or an organic cation may be prepared by reacting the appropriate compound of formula I wherein R^1 is an alkali metal ion with an appropriate transition metal salt or organic salt.

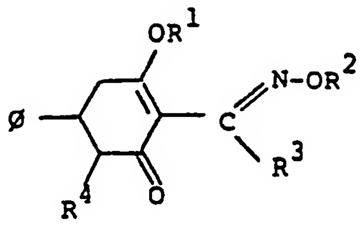
Accordingly, in a further aspect the invention provides a process for the preparation of a compound of formula I, as hereinbefore defined, which process comprises:

reacting 2-acyl-5-(aryl)cyclohexane-1,3-dione derivative of formula XIII with an alkoxyamine derivative of formula XVII to give a compound of the invention of formula II or reacting the 2-acyl-5-(aryl)cyclohexane-1,3-dione derivative of formula XIII with hydroxylamine and alkylating the oxime intermediate of formula XVIII with an alkylating agent of formula XIX, wherein L is a leaving group, to give a compound of the invention of formula II; and optionally

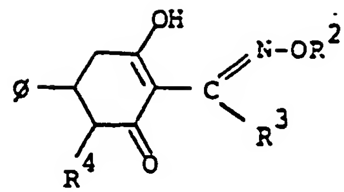
reacting the compound of the invention of formula II with a compound of formula XX, wherein L is a leaving group, to give a compound of the invention of formula I.

The structures of the compounds described above are detailed on the following pages wherein Ø represents the group





I



II

CH_3COCH_3

IVa

$CH_3COCH_2R^4$

IVb

CH_3CO_2R

IVc

Ø-CHO

V

Ø-$CH=CH-COCH_3$

VIa

Ø-$CH=CR^4-COCH_3$

VIb

Ø-$CH=C(CO_2R)_2$

VIc

Ø-$CH=CH-CO_2R$

VId

$R^4CH(CO_2R)_2$

VIIa

$CH_2(CO_2R)_2$

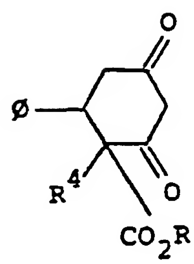
VIIb

$R^4CH_2CO_2R$

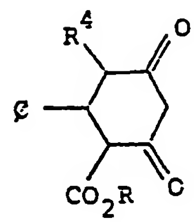
VIIc

$CH_3COCHR^4CO_2R$

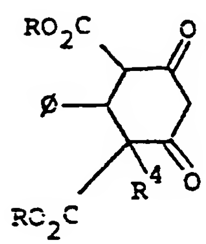
VIId



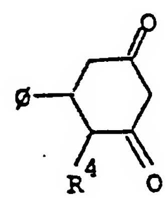
VIIIa



VIIIb



VIIIc



IX

$(R^3CO)_2O$

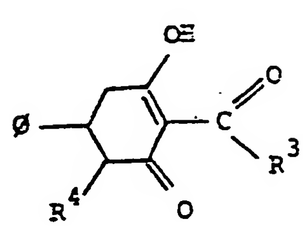
X

R^3CO_2M

XI

ROM

XII



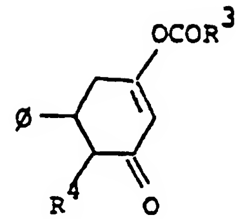
XIII

R^3CO_2H

XIV

R^3COhal

XV



XVI

H_2NOR^2

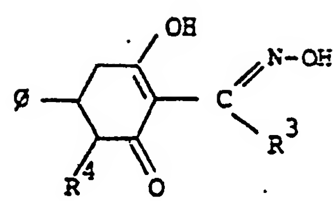
XVII

R^2L

XIX

R^1L

XX

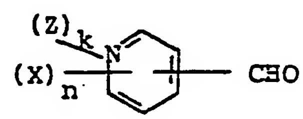


XVIII

Certain of the intermediate compounds of formulae V, VIa, VIb, VIc, VId, VIIIa, VIIIb, VIIIc, IX, XIII, XVI and XVIII are novel compounds and therefore in further embodiments the invention provides novel compounds of formulae V, VIa, VIb, VIc, VId, VIIIa, VIIIb, VIIIc, IX, XIII, XVI and XVIII and processes for the preparation thereof.

For example, the tri- and tetra-substituted pyridine carboxaldehydes of formula V used in the preparation of the compounds of the invention of formula I are novel compounds.

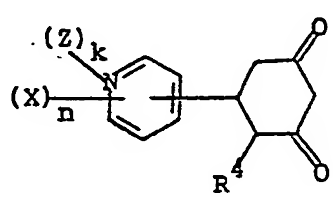
Accordingly, in another aspect the invention provides a compound of formula V



V

where Z, k and X are as hereinbefore defined and n is an integer selected from 3 and 4.

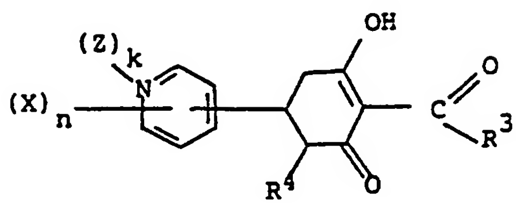
In another aspect the invention provides a compound of formula IX



IX

wherein Z, k, n, X and R^4 may have any of the values hereinbefore defined.

In another aspect the invention provides a compound of formula XIII



XIII

wherein Z, k, n, X, R^3 and R^4 may have any of the values hereinbefore defined.

The compounds of formula I are active as herbicides and therefore, in a further aspect the invention provides a process for severely damaging or killing unwanted plants which process comprises applying to the plants, or to the growth medium of the plants, an effective amount of a compound of formula I as hereinbefore defined.

Generally speaking the compounds of formula I are herbicidally effective against a variety of plants. However, certain of the compounds of the invention are selectively active against monocotyledonous plants, dicotyledonous plants being relatively unaffected by rates of application of the compounds of the invention which are severely damaging or lethal to other plant species.

Moreover, certain of the compounds of formula I are selectively active within the group of monocotyledonous plants and may be used at a rate sufficient to control monocotyledonous weeds in cultivated crops, especially wild grasses in cereal crops. Certain of such compounds of the invention are especially useful in the control of wild grasses such as wild oats and rye grass in crops of cultivated monocotyledonous plants such as wheat, barley and other varieties of cereals.

Accordingly, in yet a further aspect the invention provides a process for controlling monocotyledonous weeds in cultivated crops, especially wild grasses in cereal crops such as wheat, which process comprises applying to the crop, or to the growth medium of the crop, a compound of formula I, as hereinbefore defined, in an amount sufficient to severely damage or kill the weeds but insufficient to damage the crop substantially.

Surprisingly, it has been found that the 5-(pyridyl)cyclohexan-1,3-dione derivatives of the present invention in which the pyridine ring has three or four substituents, that is compounds in which the pyridine ring is either tetra- or fully substituted, in general show a significantly higher level of herbicidal activity than those compounds of the invention in which the pyridine ring has one or two substituents. Therefore, the preferred compounds of the present invention are those in which the pyridine ring has three or four substituents.

The compounds of formula I may be applied directly to the plant (post-emergence application) or to the soil before the emergence of the plant (pre-emergence application). However, the compounds are, in general, more effective when applied to the plant post-emergence.

The compounds of formula I may be used on their own to inhibit the growth of, severely damage, or kill plants but are preferably used in the form of a composition comprising a compound of the invention in admixture with a carrier comprising a solid or liquid diluent. Therefore, in yet a further aspect the invention provides growth inhibiting, plant damaging, or plant killing compositions comprising a compound of formula I as hereinbefore defined and an agri-

culturally acceptable carrier therefor.

Certain of the compounds of formula I exhibit useful plant growth regulating activity. For example, while compounds of formula I are selectively active herbicides against wild grasses in crops of cultivated plants at some rates of application they exhibit plant growth regulating effects in said crops.

Plant growth regulating effects may be manifested in a number of ways. For example, suppression of apical dominance, stimulation of auxiliary bud growth stimulation of early flowering and seed formation, enhancement of flowering and increase in seed yield, stem thickening, stem shortening and tillering. Plant growth regulating effects shown in compounds of the invention may include, for example, tillering and stem shortening in crops such as wheat and barley.

Accordingly in a still further aspect the invention provides a process for regulating the growth of a plant which process comprises applying to the plant, to the seed of the plant, or to the growth medium of the plant, an effective amount of a compound of formula I, as hereinbefore defined.

To effect the plant growth regulating process of the present invention the compounds of formula I may be applied directly to the plant (post-emergence application) or to the seed or soil before the emergence of the plant (pre-emergence) application.

The compounds of formula I may be used on their own to regulate the growth of plants but in general are preferably used in the form of a composition comprising a compound of the invention in admixture with a carrier comprising a solid or liquid diluent. Therefore, in a still further aspect the invention provides plant growth regulating compositions comprising a compound of formula I as hereinbefore defined and an agriculturally acceptable carrier therefor.

The compositions of the present invention may be in the form of solids, liquids or pastes. The compositions include both dilute compositions which are ready for immediate use and concentrated compositions which may require dilution before use. Therefore, the concentration of the active ingredient in the compositions of the present invention will vary depending on the types of formulation and whether the composition is ready for use such as, for example, a dust formulation or an aqueous emulsion or whether the composition is a concentrate such as, for example, an emulsifiable concentrate or a wettable powder, which is suitable for dilution before use. In general the compositions of the present invention comprise from 1 ppm to 99% by weight of active ingredient.

The solid compositions may be in the form of powders, dusts, pellets, grains, and granules wherein the active ingredient is mixed with a solid diluent. Powders and dusts may be prepared by mixing or grinding the active ingredient with a solid carrier to give a finely divided composition. Granules, grains and pellets may be prepared by bonding the active ingredient to a solid carrier, for example, by coating or impregnating the preformed granular solid carrier with the active ingredient or by agglomeration techniques.

Examples of solid carriers include: mineral earths and clays such as, for example, kaolin, bentonite, kieselguhr, Fuller's earth, Attaclay, diatomaceous earth, bole, loess, talc, chalk, dolomite, limestone, lime, calcium carbonate, powdered magnesia, magnesium oxide, magnesium sulfate, gypsum, calcium sulfate, pyrophyllite, silicic acid, silicates and silica gels; fertilizers such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate and urea; natural products

of vegetable origin such as, for example, grain meals and flours, bark meals, wood meals, nutshell meals and cellulosic powders; and synthetic polymeric materials such as, for example, ground or powdered plastics and resins.

Alternatively, the solid compositions may be in the form of dispersible or wettable dusts, powders, granules or grains wherein the active ingredient and the solid carrier are combined with one or more surface active agents which act as wetting, emulsifying and/or dispersing agents to facilitate the dispersion of the active ingredient in liquid.

Examples of surface active agents include those of the cationic, anionic and non-ionic type. Cationic surface active agents include quaternary ammonium compounds, for example, the long chain alkylammonium salts such as cetyltrimethylammonium bromide. Anionic surface active agents include: soaps or the alkali metal, alkaline earth metal and ammonium salts of fatty acids; the alkali metal, alkaline earth metal and ammonium salts of ligninsulfonic acid; the alkali metal, alkaline earth metal and ammonium salts of arylsulfonic acids including the salts of naphthalenesulfonic acids such as butylnaphthalenesulfonic acid, the di- and tri-isopropylnaphthalenesulfonic acids, the salts of the condensation products of sulfonated naphthalene and naphthalene derivatives with formaldehyde, the salts of the condensation products of sulfonated naphthalene and naphthalene derivatives with phenol and formaldehyde, and the salts of alkylarylbenzenesulfonic acids such as dodecylbenzenesulfonic acid; the alkali metal, alkaline earth metal and ammonium salts of the long chain mono esters of sulfuric acid or alkylsulfates such as laurylsulfate and the mono esters of sulfuric acid with fatty alcohol glycol ethers. Nonionic sur-

face active agents include: the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol and cetyl alcohol; the condensation products of ethylene oxide with phenols and alkylphenols such as isooctylphenol, octylphenol and nonylphenol; the condensation products of ethylene oxide with castor oil; the partial esters derived from long chain fatty acids and hexitol anhydrides, for example sorbitan monolaurate, and their condensation products with ethylene oxide; ethylene oxide/propylene oxide block copolymers; lauryl alcohol polyglycol ether acetal; and the lecithins.

The liquid compositions may comprise a solution or dispersion of the active ingredient in a liquid carrier optionally containing one or more surface active agents which act as wetting, emulsifying and/or dispersing agents. Examples of liquid carriers include: water; mineral oil fractions such as, for example, kerosene, solvent naptha, petroleum, coal tar oils and aromatic petroleum fractions; aliphatic, cycloaliphatic and aromatic hydrocarbons such as, for example, paraffin, cyclohexane, toluene, the xylenes, tetrahydronaphthalene and alkylated naphthalenes; alcohols such as, for example, methanol, ethanol, propanol, isopropanol, butanol, cyclohexanol and propylene glycol; ketones such as, for example, cyclohexanone and isophorone; and strongly polar organic solvents such as, for example, dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone and sulfolane.

A preferred liquid composition comprises an aqueous suspension, dispersion or emulsion of the active ingredient which is suitable for application by spraying, atomizing or watering. Such aqueous compositions are generally prepared by mixing concentrated compositions with water. Suitable concentrated compositions include

emulsion concentrates, pastes, oil dispersions, aqueous suspensions and wettable powders. The concentrates are usually required to withstand storage for prolonged periods and after such storage to be capable of dilution with water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. The concentrates conveniently contain from 20 to 99%, preferably 20 to 60%, by weight of active ingredient.

Emulsion or emulsifiable concentrates are conveniently prepared by dissolving the active ingredient in an organic solvent containing one or more surface active agents. Pastes may be prepared by blending the finely divided active ingredient with a finely divided solid carrier, one or more surface active agents and optionally an oil. Oil dispersions may be prepared by grinding together the active ingredient, a hydrocarbon oil, and one or more surface active agents. Aqueous suspension concentrates may conveniently be prepared by ball milling a mixture of the active ingredient, water, at least one surface active agent and preferably at least one suspending agent. Suitable suspending agents include: hydrophilic colloids such as, for example, poly(N-vinylpyrrolidone), sodium carboxymethylcellulose and the vegetable gums gum acacia and gum tragacanth; hydrated colloidal mineral silicates such as, for example, montmorillonite, beidellite, nontronite, hectorite, saponite, sauconite and bentonite; other cellulose derivatives; and poly(vinyl alcohol). Wettable powder concentrates may conveniently be prepared by blending together the active ingredient, one or more surface active agents, one or more solid carriers and optionally one or more suspending agents and grinding the mixture to give a powder having the required

particle size.

The aqueous suspensions, dispersions or emulsions may be prepared from the concentrated compositions by mixing the concentrated compositions with water optionally containing surface active agents and/or oils.

It should be noted that the compounds of the invention of formula I wherein R^1 is hydrogen are acidic. Therefore, the compounds of formula I may be formulated and applied as the salts of organic or inorganic bases. In formulating and employing the compounds of formula I in the form of their salts either the salts per se, that is the compounds of formula I wherein R^1 is an inorganic or an organic cation, may be used in the formulation or the compounds of formula I wherein R^1 is hydrogen may be used in the formulation and the salts generated in situ by the use of the appropriate organic or inorganic base.

The mode of application of the compositions of the invention will depend to a large extent on the type of composition used and the facilities available for its application. solid compositions may be applied by dusting or any other suitable means for broadcasting or spreading the solid. Liquid compositions may be applied by spraying, atomizing, watering, introduction into the irrigation water, or any other suitable means for broadcasting or spreading the liquid.

The rate of application of the compounds of the invention will depend on a number of factors including, for example, the compound chosen for use, the identity of the plants whose growth is to be inhibited the formulations selected for use and whether the compound is to be applied for foliage or root uptake. As a general guide, however, an application rate of from 0.005 to 20 kilograms per hectare is suitable while from 0.01 to 5.0 kilograms per hectare may be preferred.

The compositions of the invention may comprise, in addition to one or more compounds of the invention, one or more compounds not of the invention but which possess biological activity. For example, as hereinbefore indicated the compounds of the invention are in general substantially more effective against monocotyledonous plants or grass species than against dicotyledonous plants or broad-leaved species. As a result, in certain applications the herbicial use of the compounds of the invention alone may not be sufficient to protect a crop. Accordingly in yet a still further embodiment the invention provides a herbicidal composition comprising a mixture of at least one herbicidal compound of formula I as hereinbefore defined with at least one other herbicide.

The other herbicide may be any herbicide not having the formula I. It will generally be a herbicide having a complementary action. For example, one preferred class is of mixtures comprising a herbicide active against broad-leaved weeds. A second preferred class is of mixtures comprising a contact herbicide.

Example of useful complementary herbicides include:

A. benzo-2,1,3-thiadiazin-4-one-2,2-dioxides such as 3-isopropylbenzo-2,1,3-thiadiazin-4-one-2,2-dioxide (common name bentazon);

B. hormone herbicides and in particular the phenoxyalkanoic acids such as 4-chloro-2-methylphenoxy acetic acid (common name MCPA), 2-(2,4-dichlorophenoxy)propionic acid (common name dichlorprop), 2,4,5-trichlorophenoxyacetic acid (common name 2,4,5-T), 4-(4-chloro-2-methylphenoxy)butyric acid (common name MCPB), 2,4-dichlorophenoxyacetic acid (common name 2,4-D), 4-(2,4-dichlorophenoxy)butyric

acid (common name 2,4-DB), 2-(4-chloro-2-methylphenoxy)propionic acid (common name mecoprop), and their derivatives (eg salts, esters, amides and the like);

C. 3-[4-(4-halophenoxy)phenyl]-1,1-dialkylureas such as 3-[4-(4-chlorophenoxy)phenyl]-1,1-dimethylurea (common name chloroxuron);

D. dinitrophenols and their derivatives (eg acetates) such as 2-methyl-4,6-dinitrophenol (common name DNOC), 2-tertiarybutyl-4,6-dinitrophenol (common name dinoterb), 2-secondarybutyl-4,6-dinitrophenol (common name dinoseb) and its ester dinoseb acetate;

E. dinitroaniline herbicides such as N',N'-diethyl-2,6-dinitro-4-trifluoromethyl-m-phenylenediamine (common name dinitramine), 2,6-dinitro-N,N-dipropyl-4-trifluoromethylaniline (common name trifluralin) and 4-methylsulfonyl-2,6-dinitro-N,N-dipropylaniline (common name nitralin);

F. phenylurea herbicides such as N'-(3,4-dichlorophenyl)-N,N-dimethylurea (common name diruon), N,N-dimethyl-N'-[3-(trifluoromethyl)phenyl]urea (common name fluometuron) and N'-(4-isopropyl phenyl)-N,N-dimethylurea;

G. phenylcarbamoyloxyphenylcarbamates such as 3-[(methoxycarbonyl)amino]phenyl (3-methylphenyl)-carbamate (common name phenmedipham) and 3-[(ethoxycarbonylamino]phenyl phenylcarbamate (common name desmedipham);

H. 2-phenylpyridazin-3-ones such as 5-amino-4-chloro-2-phenylpyridazin-3-one (common name pyrazon);

I. uracil herbicides such as 3-cyclohexyl-5,6-trimethyleneuracil (common name lenacil), 5-bromo-3-sec-butyl-6-methyluracil (common name bromacil) and 3-tert-butyl-5-chloro-6-methyluracil (common name terbacil);

J. triazine herbicides such as 2-chloro-4-ethylamino-6-(iso-propylamino)-1,3,5-triazine (common name atrazine), 2-chloro-4,6-di(ethylamino)-1,3,5-triazine (common name simazine) and 2-azido-4-(iso-propylamino)-6-methylthio-1,3,5-triazine (common name aziproptryne);

K. 1-alkoxy-2-alkyl-3-phenylurea herbicides such as 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (common name linuron), 3-(4-chlorophenyl)-1-methoxy-1-methylurea (common name monolinuron) and 3-(4-bromo-4-chlorophenyl)-1-methoxy-1-methylurea (common name chlorobromuron);

L. thiocarbamate herbicides such as S-propyl dipropylthiocarbamate (common name verolate);

M. 1,2,4-triazin-5-one herbicides such as 4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazine-5-one (common name metamitron) and 4-amino-6-tert-butyl 4,5-dihydro-3-methylthio-1,2,4-triazin-5-one (common name metribuzin);

N. benzoic acid herbicides such as 2,3,6-trichlorobenzoic acid (common name 2,3,6-TBA), 3,6-dichloro-2-methyoxybenzoic acid (common name dicamba) and 3-amino-2,5-dichlorobenzoic acid (common name chloramben);

O. anilide herbicides such as N-butoxymethyl-α-chloro-2',6'-diethylacetanilide (common name butachlor), the corresponding N-methoxy compound (common name alachlor), the corresponding N-iso-propyl compound (common name propachlor) and 3',4'-dichloro-propionanilide (common name propanil);

P. dihalobenzonitrile herbicides such as 2,6-dichloro-benzonitrile (common name dichlobenil), 3,5-dibromo-4-hydroxybenzonitrile (common name bromoxynil) and 3,5-diiodo-4-hydroxybenzonitrile (common name ioxynil).

Q. Haloalkanoic herbicides such as 2,2-dichloro-propionic acid (common name dalapon), trichloro-acetic acid (common name TCA) and salts thereof;

R. diphenylether herbicides such as 4-nitrophenyl 2-nitro-4-trifluoromethylphenyl ether (common name fluorodifen), methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate (common name bifenox), 2-nitro-5-(2-chloro-4-trifluoromethylphenoxy)benzoic acid and 2-chloro-4-trifluoromethylphenyl 3-ethoxy-4-nitro-phenyl ether;

S. N-(heteroarylaminocarbonyl)benzenesulfonamides such as 2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]benzenesulfonamide (commonly known as DPX 4189); and

T. miscellaneous herbicides including N,N-dimethyl-diphenylacetamide (common name diphenamid), N-(1-naphthyl)phthalamic acid (common name naptalam) and 3-amino-1,2,4-triazole.

Examples of useful contact herbicides include:

U. bipyridylium herbicides such as those in which the active entity is the 1,1'-dimethyl-4,4'-dipyridylium ion (common name paraquat) and those in which the active entity is the 1,1'-ethylene-2,2'-dipyridylium ion (common name diquat);

V. organoarsenical herbicides such as monosodium methanearsonate (common name MSMA); and

W. amino acid, herbicides such as N-(phosphonomethyl)-glycine (common name glyphosate) and its salts and esters.

The invention is now illustrated by, but in no way limited to, the following Examples wherein all temperatures quoted are in degrees Centigrade.

Example 1

Preparation of 3-cyanopyrid-2-ones

a) 3-Cyano-6-methylpyrid-2-one was prepared from 3-oxo-butyraldehyde-1-dimethylacetal and cyanoacetamide following the procedure of Binovi and Arlt (J. Org. Chem. 26, 1656, 1961).

b) 3-Cyano-6-hydroxy-4-methylpyrid-2-one was prepared from ethyl acetoacetate and cyanoacetamide following the procedure of Bobbitt and Scola (J. Org. Chem. 25, 560, 1960). 3-Cyano-4,5-dimethyl-6-hydroxypyrid-2-one was similarly prepared from ethyl methylacetoacetate and cyanoacetamide.

c) 3-Cyano-6-methyl-4-trifluoromethylpyrid-2-one was prepared from 1,1,1-trifluoroacetylacetone and cyanoacetamide following the procedure of Kametani and Sato (Yakugaku Kenkyu 34, 117, 1962). 3-Cyano-4,6-dimethylpyrid-2-one and 3-cyano-4,5,6-trimethylpyrid-2-one were similarly prepared from acetylacetone and cyanoacetamide, and 3-methylpentan-2,4-dione and cyanoacetamide respectively.

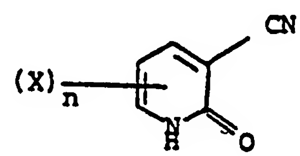
d) 5-Chloro-3-cyano-4,6-dimethylpyrid-2-one was prepared from 3-cyano-4,6-dimethylpyrid-2-one following essentially the same procedure as that described by Gershon, Dittmer and Braun (J. Org. Chem., 26, 1874, 1961) for the chlorination of 6-methyluracil.

e) 5-Bromo-3-cyano-4,6-dimethylpyrid-2-one was prepared from 3-cyano-4,6-dimethylpyrid-2-one following essentially the same procedure as that described by

Comins and Lye (J. Org. Chem., 41, 2065, 1976) for the bromination of 1,3-dimethyl-2-pyridone.

All products were characterized by proton nuclear magnetic resonance spectroscopy and physical data and spectroscopic data are recorded in Table 2.

TABLE 2



$(X)_n$	Appearance	Proton Chemical Shift δ in ppm ($DMSO-d_6$)
$6-CH_3$	Colourless solid, mp 290°	Not recorded
$4-CH_3-6-OH$	Colourless solid, mp >260°	2.32(3H,s); 5.82(1H,s); 8.67(2H,brs).
$4-CF_3-6-CH_3$	Colourless solid, mp 234°	2.38(3H,s); 6.47(1H,s); 8.78(1H,s).
$4,5-(CH_3)_2-6-OH$	Cream solid, mp 236-40°	1.89(3H,s); 2.21(3H,s); 6.05(2H,brs)
$4,6-(CH_3)_2$	Colourless solid, mp 286-88°	2.23(3H,s); 2.30(3H,s); 6.14(1H,s); 12.16(1H,s).

TABLE 2 continued

$(X)_n$	Appearance	Proton Chemical Shift δ in ppm (DMSO-d_6)
4,6-$(CH_3)_2$-5-Cl	Light brown needles, mp 210° (sublimes)	2.36(3H,s); 2.41(3H,s); 3.31(1H,brs).
4,6-$(CH_3)_2$-5-Br	Colourless solid, mp 267°	2.37(3H,s); 2.46(3H,s); 12.79(1H,s).
4,5,6-$(CH_3)_3$	Colourless solid, mp >260°	1.92(3H,s); 2.24(3H,s); 2.3(3H,s); 11.98(1H,brs).

Example 2

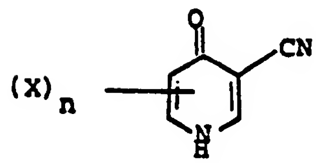
Preparation of 3-cyanopyrid-4-ones

a) 3-Cyano-2,6-dimethylpyrid-4-one was prepared from 3-aminocrotononitrile and diketene following the procedure of Kato et al (Yakugaku Zasshi 91, 740, 1971).

b) 5-Chloro-3-cyano-2,6-dimethylpyrid-4-one was prepared from 3-cyano-2,6-dimethylpyrid-4-one following essentially the same procedure as that described by Gershon, Dittmer and Braun (J. Org. Chem., 26, 1874, 1961) for the chlorination of 6-methyluracil.

The products were characterized by proton nuclear magnetic resonance spectroscopy and physical data and spectroscopic data are recorded in Table 3.

TABLE 3



$(X)_n$	Appearance	Proton Chemical Shift δ in ppm ($DMSO-d_6$)
$2,6-(CH_3)_2$	Colourless solid, mp 299°	1.92(3H,s); 2.12(3H,s); 5.74(1H,s); 11.3(1H,s).
$2,6-(CH_3)_2$-5-Cl	Colourless solid, mp >260°	2.36(3H,s); 2.42(3H,s); 12.23(1H,brs).

Example 3

Preparation of 3-cyanopyridines

The 3-cyanopyridines were prepared by one of the following methods:

a) 2-Chloro-3-cyano-4,6-dimethylpyridine was prepared from 3-cyano-4,6-dimethylpyrid-2-one and phosphorus oxychloride following the procedure of Kametani and Sato (Yakugaka Kenyu 34, 117, 1962).

b) i) n-Pentyl 4-hydroxy-6-methylpyrid-2-one-3-carboxylate was prepared from ethyl 3-aminocrotonate, diethyl malonate, n-pentyl alcohol and sodium following the procedure of Bruce and Perez-Medina (J. Amer. Chem. Soc. 69, 2571,

1947), and was obtained as a white solid, mp 142-44°. Pmr spectrum (δ in ppm; acetone-d_6 0.77-1.87 (9H,m); 2.31 (3H,s); 4.31 (2H,t); 5.80 (1H,s); OH and NH not observed.

(ii) 4-Hydroxy-6-methylpyrid-2-one-3-carboxamide was prepared from n-pentyl 4-hydroxy-6-methylpyrid-2-one-3-carboxylate and ethanolic ammonia following the procedure of Bruce and Perez-Medina (J. Amer. Chem. Soc. 69, 2571, 1947), and was obtained as a white solid, mp 255°. Pmr spectrum (δ in ppm: DMSO-d_6): 2.17 (3H,s); 5.85 (1H,s); OH and NH not observed.

(iii) 3-Cyano-2,4-dichloro-6-methylpyridine was prepared from 4-hydroxy-6-methylpyrid-2-one-3-carboxamide and phosphorus oxychloride following essentially the same procedure as that described in Method a) above.

c) 3-Cyano-6-methylpyridine was prepared by hydrogenation of 2-chloro-3-cyano-6-methylpyridine following essentially the same procedure as that described by Bobbitt and Scola (J. Org. Chem. 25, 560, 1960).

d) 3-Cyano-4,6-dimethyl-2-methoxypyridine was prepared by reacting 2-chloro-3-cyano-4,6-dimethylpyridine and sodium methoxide in refluxing methanol

e) 3-Cyano-2-ethoxy-4,6-dimethylpyridine was prepared by reacting 3-cyano-4,6-dimethylpyrid-2-one with triethyloxonium tetrafluoroborate in dichloromethane.

f) (i) 3-Cyano-4,6-dimethylpyrid-2-thione was prepared from 3-cyano-4,6-dimethylpyridine and thiourea following the procedure of Guerrara,

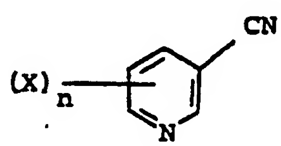
Siracusa and Tornetta (Il, Farmaco Ed. Sc. 31, 21, 1975), and was obtained as yellow needles, mp 245-250°.

(ii) 3-Cyano-4,6-dimethyl-2-methylthiopyridine was prepared by methylation of 3-cyano-4,6-dimethylpyrid-2-thione using the method of Renault (Am. Chim. 10, 135, 1955).

g) 3-Cyano-2,4,6-trimethylpyridine was prepared from 3-aminocrotonitrile and acetylacetone following the procedure of Kato and Noda (Chem. Pharm. Bull. 24, 303, 1976).

All products were characterized by proton nuclear magnetic resonance spectroscopy and method of preparation, physical data and spectroscopic data are recorded in Table 4.

TABLE 4



$(X)_n$	Me-thod	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
2-Cl-4,6-$(CH_3)_2$	a	White solid; mp 98-100°	2.55(3H,s); 2.57(3H,s); 7.10(1H,s).
2-Cl-6-CH_3	a	White solid; mp 120°	2.60(3H,s); 7.20(1H,d); 7.84(1H,d).
2,6-Cl_2-4-CH_3	a	-	2.61(3H,s); 7.35(1H,s).

TABLE 4 continued

$(X)_n$	Method	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
2-Cl-6-CH_3-4-CF_3	a	Oil	2.76(3H,s); 7.55(1H,s).
4-Cl-2,6-$(CH_3)_2$	a	White solid, mp 78-80°	2.57(3H,s); 2.75(3H,s); 7.17(1H,s).
2,6-Cl_2-4,5-$(CH_3)_2$	a	Yellow solid, mp 76°C	2.38(3H,s); 2.58(3H,s).
2-Cl-4,6-$(CH_3)_2$	a	White solid, mp 98-100°	2.55(3H,s); 2.57(3H,s); 7.10(1H,s).
4,5-Cl_2-2,6-$(CH_3)_2$	a	White solid, mp 128°	2.69(3H,s); 2.71(3H,s).
2,5-Cl_2-4,6-$(CH_3)_2$	a	Brown solid, mp 82°	2.63(3H,s); 2.68(3H,s).
5-Br-2-Cl-4,6-$(CH_3)_2$	a	-	2.56(6H,s).
2-Cl-4,5,6-$(CH_3)_3$	a	-	2.26(3H,s); 2.51(3H,s); 2.56(3H,s).
2,4-Cl_2-6-CH_3	b	White solid, mp 101°	2.62(3H,s); 7.30(1H,s).
6-CH_3	c	White solid, mp 89°	2.60(3H,s); 7.23(1H,d); 7.82(1H,dofd); 8.68 (1H,d).
2-CH_3O-4,6-$(CH_3)_2$	d	White solid, mp 97-99°	2.44(6H,s); 4.00(3H,s); 6.67(1H,s).
2-CH_3O-6-CH_3	d	-	2.5(3H,s); 4.03(3H,s); 6.82(1H,s); 7.73(1H,s).

TABLE 4 continued

$(X)_n$	Method	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
2,6-(CH_3O)-4-CH_3	d	-	2.42(3H,s); 3.99(3H,s); 4.02(3H,s); 6.21(1H,s).
2-CH_3O-6-CH_3-4-CF_3	d	White solid, mp 73-74°	2.60(3H,s); 4.09(3H,s); 7.09(1H,s).
5-Cl-2-CH_3O-4,6-$(CH_3)_2$	d	White solid, mp 91-93°	2.52(3H,s); 2.57(3H,s); 4.00(3H,s).
2-CH_3O-4,5,6-$(CH_3)_3$	d	-	2.14(3H,s); 2.41(3H,s); 2.46(3H,s); 3.97(3H,s).
2-C_2H_5O-4,6-$(CH_3)_2$	e	White solid, mp 88°	1.41(3H,t); 2.43(6H,s); 4.45(2H,q); 6.66(1H,s).
4,6-$(CH_3)_2$-2-CH_3S	f	Yellow solid, mp 87°	2.4(3H,s); 2.48(3H,s); 2.57(3H,s); 7.08(1H,s).
2,4,6-$(CH_3)_3$	g	White solid, mp 48-50°	2.48(3H,s); 2.54(3H,s); 2.71(3H,s); 6.95(1H,s).

Example 4

Preparation of pyridine-3-carboxaldehydes

a) 2,4,6-Trimethoxypyridine-3-carboxaldehyde was prepared by the following procedure:

i) 2,6-Dichloropyridine-1-oxide was prepared from 2,6-dichloropyridine following the procedure of Rousseau and Robins (J. Het. Chem. 2, 196, 1965), and was obtained as colourless

crystals, mp 142°.

ii) 2,6-Dichloro-4-nitropyridine-1-oxide was prepared by nitrating 2,6-dichloropyridine-1-oxide by the method of Rousseau and Robins (J. Het. Chem. 2, 196, 1965), and was obtained as a light yellow solid, mp 177-78°.

iii) 2,4,6-Trimethoxypyridine-1-oxide was prepared by reacting 2,6-dichloro-4-nitropyridine-1-oxide and sodium methoxide by the method of Johnson, Katrizky and Viney (J. Chem. Soc. B, 1211, 1967), and was obtained as white needles, mp 108-09°.

iv) 2,4,6-Trimethoxypyridine was prepared by reacting 2,4,6-trimethoxypyridine-1-oxide and phosphorus trichloride by the method of Johnson, Katrizky and Viney (J. Chem. Soc. B, 1211, 1967), and was obtained as a colourless solid. Pmr spectrum (δ in ppm; $CDCl_3$): 3.77 (3H,s); 3.87 (6H,s); 5.85 (2H,s).

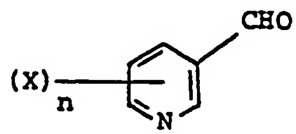
v) 2,4,6-Trimethoxypyridine-3-carboxaldehyde was prepared from 2,4,6-trimethoxypyridine by Vilsmeir formylation using the same procedure as that described by Kompis et al (Eur. J. Med. Chem. -·Chimica Ther. 12, 531, 1977) for the formylation of 2,6-dimethoxypyridine.

b) All other pyridine-3-carboxaldehydes were prepared by reacting the appropriate 3-cyanopyridine with diisobutylaluminium hydride following essentially the same procedure as that described by Beak et al (J. Org. Chem. 45, 1354, 1980) for the reduction of 3-cyano-2-methoxy-6-methylpyridine.

All products were characterized by proton nuclear

magnetic resonance spectroscopy and physical data and spectroscopic data are recorded in Table 5.

TABLE 5



$(X)_n$	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
6-CH_3	Orange oil	2.6(3H,s); 7.24(1H,d); 7.99 (1H,m); 8.84(1H,d); 9.96 (1H,s).
2-Cl-6-CH_3	White solid, mp 67°	2.64(3H,s); 7.25(1H,d); 8.14(1H,d); 10.42(1H,s).
2-OCH_3-6-CH_3	White solid, mp 39°	2.50(3H,s); 4.04(3H,s); 6.83(1H,d); 7.98(1H,d); 10.30(1H,s).
2,6-Cl_2-4-CH_3	-	2.61(3H,s); 7.18(1H,s); 10.47(1H,s).
2,6-$(OCH_3)_2$-4-CH_3	-	2.57(3H,s); 3.93(3H,s); 4.02(3H,s); 6.09(1H,s); 10.37(1H,s).
2,4-Cl_2-6-CH_3	Colourless needles, mp 62-3°	2.59(3H,s); 7.25(1H,s); 10.44(1H,s).
2-Cl-4-CF_3-6-CH_3	Oil	2.69(3H,s); 7.50(1H,s); 10.43(1H,s).

TABLE 5 continued

$(X)_n$	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
2-OCH_3-4-CF_3-6-CH_3	Oil	2.57(3H,s); 4.07(3H,s); 7.10(1H,s); 10.39(1H,s).
4-Cl-2,6-$(CH_3)_2$	White solid, mp 40-3°	2.55(3H,s); 2.77(3H,s); 7.14(1H,s); 10.60(1H,s).
2,6-Cl_2-4,5-$(CH_3)_2$	Low-melting pale yellow solid	2.35(3H,s); 2.58(3H,s); 10.50(1H,s).
2-Cl-4,6-$(CH_3)_2$	White solid, mp 45-6°	2.55(3H,s); 2.59(3H,s); 7.03(1H,s); 10.54(1H,s).
2-OCH_3-4,6-$(CH_3)_2$	-	2.39(3H,s); 2.48(3H,s); 3.97(3H,s); 6.54(1H,s); 10.4(1H,s).
2-SCH_3-4,6-$(CH_3)_2$	Yellow solid, mp 72-3°	2.08(3H,s); 2.18(3H,s); 6.80(1H,s); 10.35(1H,s).
4,5-Cl_2-2,6-$(CH_3)_2$	White solid, mp 58°	2.70(3H,s); 2.74(3H,s); 10.58(1H,s).
2,5-Cl_2-4,6-$(CH_3)_2$	White solid, mp 90°	2.67(6H,s); 10.5(1H,s).
5-Br-2-Cl-4,6-$(CH_3)_2$	-	2.68(3H,s); 2.73(3H,s); 10.42(1H,s).
2-OCH_3-5-Cl-4,6-$(CH_3)_2$	Oil	2.57(3H,s); 2.66(3H,s); 4.00(3H,s); 10.45(1H,s).
2,4,6-$(CH_3)_3$	Yellow oil	2.50(3H,s); 2.54(3H,s); 2.76(3H,s); 6.88(1H,s); 10.54(1H,s).

TABLE 5 continued

$(X)_n$	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
2-Cl-4,5,6-$(CH_3)_3$	-	2.25(3H,s); 2.52(3H,s); 2.56(3H,s); 10.51(1H,s).
2-OCH_3-4,5,6-$(CH_3)_3$	-	2.12(3H,s); 2.39(3H,s); 2.51(3H,s); 3.97(3H,s); 10.47(1H,s).
2,4,6-$(OCH_3)_3$	Yellow oil	3.9(3H,s); 3.96(3H,s); 4.02(3H,s); 5.88(1H,s); 10.25(1H,s).

Example 5

Preparation of 1-/3-(substituted pyridyl)/but-1-en-3-ones

The 1-/3-(substituted pyridyl)/but-1-en-3-ones used in the preparation of the compounds of the invention of formula I were prepared from the appropriate pyridine-3-carboxaldehyde by one of the following methods:

a) Pyridine-3-carboxaldehyde (18.9 ml) and 1-triphenylphosphoranylidene-2-propanone (70 g) were heated at reflux in toluene for 2 hr. The solvent was evaporated and the residue was distilled at reduced pressure to give 1-(3-pyridyl)but-1-en-3-one as an oil. Pmr spectrum ($CDCl_3$; δ in ppm): 2.41 (3H,s); 6.79 (1H,d); 7.2-8.77 (4H,m); 7.52 (1H,d).

b) A solution of 4,6-dimethyl-2-methoxypyridine-3-

carboxaldehyde (5.00 g, 30.3 mmol) in acetone (150 ml) was added dropwise to a cooled mixture of acetone (150 ml) and aqueous sodium hydroxide (2%, 9 ml). The mixture was stirred at 0°C for 1-2 hours and then warmed to room temperature and stirred overnight. The acetone was evaporated under reduced pressure and additional water (100 ml) was added followed by acidification to pH 8. The mixture was extracted with dichloromethane (3 x 50 ml), which in turn was washed with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure to give a crude oil. Heating the oil to 50°C under high vacuum gave 1-[3-(4,6-dimethyl-2-methoxypyridyl)]but-1-en-3-one (6.20 g, 100%) as a pale yellow viscous oil. Proton magnetic resonance spectrum ($CDCl_3$; δ in ppm): 2.36 (3H,s); 2.38 (3H,s); 2.40 (3H,s); 3.99 (3H,s); 6.62 (1H,s); 6.97 (1H,d); 7.70 (1H,d).

The specific method used for the preparation of each 1-[3-(substituted pyridyl)]but-1-en-3-one is indicated in Example 7, Table 8.

Example 6

Preparation of 2-acyl-3-hydroxy-5-[3-(substituted pyridyl)]cyclohex-2-en-1-ones

The 2-acyl-3-hydroxy-5-[3-(substituted pyridyl)]-cyclohex-2-en-1-ones used in the preparation of the compounds of the invention of formula I were prepared from the appropriate 1-[3-(substituted pyridyl)]-but-1-en-3-one either by Method a) below which involves isolation of the intermediate 3-hydroxy-5-[3-(substituted pyridyl)]cyclohex-2-en-1-one, or by Method b) below.

a) i) Diethyl malonate (5.04 g, 31.5 mmol) was added to a solution of sodium metal (0.73 g, 31.5 mmol) in absolute ethanol (70 ml) and the mixture refluxed for 30 minutes. A mixture of 1-[3-(4,6-dimethyl-2-methoxypyridyl)]but-1-en-3-one (6.20 g, 30.0 mmol) and absolute ethanol (20 ml) was added and the mixture was heated under reflux for a period of 2 hours. An aqueous solution of sodium hydroxide (4.0 g, 30 ml of water) was added and the mixture was heated under reflux for a further 3.5 hours. The ethanol was removed by distillation and additional water (50 ml) as added. The aqueous mixture was washed with dichloromethane (2 x 100 ml), then heated to 70°C and acidified to pH 4 with concentrated hydrochloric acid. After the evolution of carbon dioxide had ceased the mixture was cooled and the precipitate collected and dried to give 3-hydroxy-5-[3-(4,6-dimethyl-2-methoxypyridyl)]cyclohex-2-en-1-one (5.50 g, 75%) as a pale brown solid, mp 190°C.

ii) 3-Hydroxy-5-[3-(4,6-dimethyl-2-methoxypyridyl)]cyclohex-2-en-1-one (1.00 g, 4.05 mmol) was dissolved in dry dimethylformamide (20 ml). Sodium hydride (107 mg, 4.45 mmol) was added and the mixture stirred at 50°C for 30 minutes.

Butyric anhydride (0.70 g, 4.45 mmol) was added and the mixture was heated at 130°C under a nitrogen atmosphere. After 1 hour the mixture was poured into water, the aqueous mixture was extracted with dichloromethane

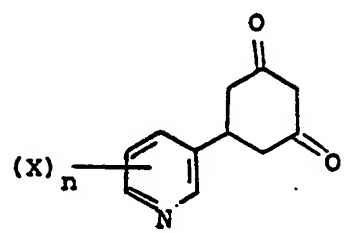
and the extract was washed with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure to give a crude product (1.00 g). Purification by column chromatography over silica gel (eluent dichloromethane) gave 2-butyryl-3-hydroxy-5-[3-(4,6-dimethyl-2-methoxypyridyl)]cyclohex-2-en-1-one (0.60 g, 47%) as an oil.

b) 1-(3-Pyridyl)but-1-en-3-one (21.3 g) and sodium diethyl malonate (1.1 equiv) were heated at reflux in absolute ethanol (200 ml) for 3 hr. The solvent was evaporated and the residue was thoroughly dried (100°C; 0.1 mmHg). Anhydrous dimethylformamide (250 ml) was added to the solid residue and the mixture was heated at 60° under nitrogen for 20 min. n-Butyric anhydride (27 ml) was added in one portion and the mixture was heated at 100° for 20 min. The solvent was evaporated by distillation under reduced pressure. The residue was boiled with an aqueous potassium hydroxide solution (4 equiv., 100 ml) for 6 hr. The hot solution was made just acid by slow addition of a dilute hydrochloric acid solution. After cooling, the mixture was extracted with ethyl acetate. The dried ($MgSO_4$) organic extract was evaporated and the residue was chromatographed over silica with ethyl acetate elution to give 3-hydroxy-5-(3-pyridyl)-2-butyryl-cyclohex-2-en-1-one as a white solid, mp 72°.

All products were characterized by proton nuclear magnetic resonance spectroscopy. Physical data and spectroscopic data for the 3-hydroxy-5-[3-(substituted pyridyl)]cyclohex-2-en-1-ones prepared according to Method a) i) above are recorded in Table 6 below. Physical data and spectroscopic data for the

2-acyl-3-hydroxy-5-[3-(substituted pyridyl)]cyclohex-2-en-1-ones prepared according to Method a) ii) and Method b) above are recorded in Table 7 below. The specific Method used for the preparation of each 2-acyl-3-hydroxy-5-[3-(substituted pyridyl)]cyclohex-2-en-1-one is indicated in Example 7, Table 8.

TABLE 6

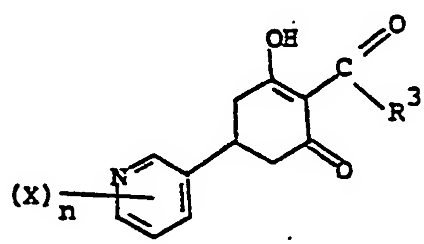


$(X)_n$	Appearance	Proton Chemical Shift δ in ppm ($DMSO-d_6$)
$2-OCH_3-6-CH_3$	Pale brown solid, mp 179°	Not recorded
$2,4,6-(OCH_3)_3$	-	1.82-2.28(2H,m); 2.62-3.19(2H,m); 3.47-4.04 (1H,m); 3.82(3H,s); 3.84(3H,s); 3.88(3H,s); 5.27(1H,s); 6.09(1H,s); 7.88(1H,brs).
$2-OCH_3-4,6-(CH_3)_2$	Brown solid, mp 190°	2.24(3H,s); 2.28(3H,s); 4.02(3H,s); 2.2-4.0(7H, m); 6.93(1H,s).
$2,4,6-(CH_3)_3$	Oil	2.32(9H,s); 2.10-4.00 (7H,m); 6.84(1H,s).

TABLE 6 continued

$(X)_n$	Appearance	Proton Chemical Shift δ in ppm (DMSO-d_6)
2-Cl-4,5,6-$(CH_3)_3$	-	1.97-4.22(5H,m); 2.20 (3H,s); 2.37(3H,s); 2.43 (3H,s); 5.38(1H,s); 11.28(1H,brs).
2-OCH_3-4,5,6-$(CH_3)_3$	-	1.85-4.05(5H,m); 2.05 (3H,s); 2.20(3H,s); 2.31 (3H,s); 3.82(3H,s); 5.29 (1H,s); 10.0(1H,brs).

TABLE 7



$(X)_n$	R^3	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
all H	n-C_3H_7	White solid mp 72°	1.00(3H,t); 1.69(2H, m); 2.66-3.61(7H,m); 7.22-8.56(4H,m); 18.33 (1H,s).

TABLE 7 continued

$(X)_n$	R^3	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
6-CH_3	n-C_3H_7	White solid, mp 63°C	0.96(3H,t); 1.44-1.84 (2H,m); 2.48(3H,s); 2.64-2.92(4H,m); 3.00 (2H,t); 3.16-3.40(1H, m); 7.08(1H,d); 7.36 (1H,m); 8.32(1H,d); 18.24(1H,s).
2-Cl-6-CH_3	n-C_3H_7	Orange oil	1.00(3H,t); 1.48-1.80 (2H,m); 2.48(3H,s); 2.52-3.12(6H,m); 3.60-3.84(1H,m); 7.08(1H, d); 7.44(1H,d); 18.24 (1H,s).
2-OCH_3-6-CH_3	n-C_3H_7	White solid, mp 90°	0.99(3H,t); 1.44-1.85 (2H,m); 2.42(3H,s); 2.57-3.20(6H,m); 3.31-3.77(1H,m); 3.95(3H, s); 6.72(1H,d); 7.26 (1H,d); 18.29(1H,s).
2,4,6-$(OCH_3)_3$	n-C_3H_7	-	0.97(3H,t); 1.68(2H,m); 2.19-2.68(2H,m); 2.85-4.1(5H,m); 3.79(3H,s); 3.87(3H,s); 3.88(3H,s); 5.89(1H,s); 18.22(1H, s).
2,6-Cl_2-4-CH_3	n-C_3H_7	Yellow oil	1.00(3H,t); 1.55-1.78 (2H,m); 2.41(3H,s); 2.44-2.73(2H,m); 3.04 (2H,t); 3.21-3.90(3H,

TABLE 7 continued

$(X)_n$	R^3	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
			m); 7.17(1H,s); 18.37 (1H,s).
2,6-$(OCH_3)_2$-4-CH_3	n-C_3H_7	-	1.03(3H,t); 1.72(2H,m); 2.18-4.00(7H,m); 2.26 (3H,s); 3.89(3H,s); 3.95(3H,s); 6.15(1H, s); 18.32(1H,s).
2,4-Cl_2-6-CH_3	n-C_3H_7	Yellow oil	1.01(3H,t); 1.51-1.91 (2H,m); 2.37-2.80(5H, m); 3.06(2H,t); 3.49-4.51(3H,m); 7.19(1H,s); 18.30(1H,s).
2-Cl-4-CF_3-6-CH_3	n-C_3H_7	Oil	1.0(3H,t); 1.69(2H,m); 2.61(3H,s); 2.4-4.0 (7H,m); 7.41(1H,s); 18.38(1H,s).
2-OCH_3-4-CF_3-6-CH_3	n-C_3H_7	Oil	1.01(3H,s); 1.71(2H,m); 2.5(3H,s); 2.4-4.0(7H, m); 4.01(3H,s); 7.00 (1H,s); 18.33(1H,s).
4-Cl-2,6-$(CH_3)_2$	n-C_3H_7	-	1.00(3H,t); 1.63(2H,m); 2.2-4.92(7H,m); 2.45 (3H,s); 2.66(3H,s); 7.00(1H,s); 18.35(1H, s).
2,6-Cl_2-4,5-$(CH_3)_2$	n-C_3H_7	Brown oil	1.04(3H,t); 1.50-1.84 (2H,m); 2.38(3H,s); 2.39(3H,s); 2.53-2.71

TABLE 7 continued

$(X)_n$	R^3	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
			(2H,m); 2.88-3.17(2H, t); 3.20-4.03(3H,m); 18.50(1H,s).
2-Cl-4,6-$(CH_3)_2$	n-C_3H_7	Oil	1.00(3H,t); 1.68(2H, q); 2.42(3H,s); 2.46 (3H,s); 2.4-3.9(7H,m); 7.0(1H,s); 18.37(1H, s).
2-OCH_3-4,6-$(CH_3)_2$	C_2H_5	-	1.16(3H,t); 2.26(3H, s); 2.37(3H,s); 2.3-3.7(7H,m); 3.93(3H,s); 6.57(1H,s); 18.27(1H, s).
2-OCH_3-4,6-$(CH_3)_2$	n-C_3H_7	Oil	1.00(3H,t); 1.57(2H, m); 2.26(3H,s); 2.37 (3H,s); 2.1-2.6(2H,m); 2.7-3.9(5H,m); 3.93 (3H,s); 6.56(1H,s); 18.31(1H,s).
2-OC_2H_5-4,6-$(CH_3)_2$	n-C_3H_7	-	1.01(3H,t); 1.37(3H, t); 1.73(2H,m); 2.25 (3H,s); 2.35(3H,s); 2.3-3.9(7H,m); 4.40 (2H,q); 6.55(1H,s); 18.34(1H,s).
2-SCH_3-4,6-$(CH_3)_2$	n-C_3H_7	Oil	1.00(3H,t); 1.48-1.82 (2H,m); 2.10-3.92(16H, m); 6.66(1H,s); 18.28 (1H,s).

TABLE 7 continued

$(X)_n$	R^3	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
4,5-Cl_2-2,6-$(CH_3)_2$	n-C_3H_7	Colourless oil	1.00(3H,t); 1.68(2H,m); 2.59(6H,s); 3.01(2H,t); 2.26-3.95(5H,m); 18.16(1H,s).
2,5-Cl_2-4,6-$(CH_3)_2$	C_2H_5	Yellow oil	1.14(3H,t); 2.17-4.26(7H,m); 2.41(3H,s); 2.52(3H,s); 18.26(1H,s).
2,5-Cl_2-4,6-$(CH_3)_2$	n-C_3H_7	Oil	0.99(3H,t); 1.43-1.94(2H,m); 2.29-4.17(13H,m); 18.40(1H,s).
5-Br-2-Cl-4,6-$(CH_3)_2$	n-C_3H_7	Brown oil	1.00(3H,t); 1.55-1.81(2H,m); 2.57(3H,s); 2.63(3H,s); 2.74-4.20(7H,m); 18.35(1H,s).
2-OCH_3-5-Cl-4,6-$(CH_3)_2$	n-C_3H_7	Oil	1.00(3H,t); 1.51-1.86(2H,m); 2.29-3.75(13H,m); 3.91(3H,s); 18.32(1H,s).
2,4,6-$(CH_3)_3$	n-C_3H_7	Oil	1.00(3H,t); 1.69(2H,m); 2.36(3H,s); 2.44(3H,s); 2.60(3H,s); 2.30-3.8(7H,m); 6.82(1H,s).
2-Cl-4,5,6-$(CH_3)_3$	n-C_3H_7	Oil	1.0(3H,t); 1.70(2H,m); 2.03-2.71(2H,m); 2.22(3H,s); 2.34(3H,s); 2.49(3H,s); 2.89-4.0(5H,m); 18.34(1H,s).

TABLE 7 continued

$(X)_n$	R^3	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
2-OCH_3-4,5,6-$(CH_3)_3$	n-C_3H_7	Oil	1.0(3H,t); 1.71(2H,q); 2.00-2.14(2H,m); 2.14(3H,s); 2.23(3H,s); 2.4(3H,s); 2.92-4.0 (5H,m); 3.92(3H,s); 18.29(1H,s).

Example 7

Preparation of the compounds of the invention of formula I

The compounds of the invention of formula I indicated in Table 8 were prepared from the appropriate 2-acyl-3-hydroxy-5-/3-(substituted pyridyl)/cyclohex-2-en-1-one and the appropriate hydroxylamine hydrochloride derivative either by Method a) or Method b) below.

a) 2-/1-(Ethoxyimino)butyl/-3-hydroxy-5-/3-(pyridyl)/-cyclohex-2-en-1-one (1)

3-Hydroxy-5-(3-pyridyl)-2-butyrylcyclohex-2-en-1-one (1.0 g) was stirred with O-ethylhydroxylamine hydrochloride (1.1 equiv) and sodium acetate trihydrate (1.1 equiv) in ethanol (30 ml) at room temperature for 12 hr. The mixture was poured into a dilute acetic acid solution, which was subsequently extracted with ether. The dried ($MgSO_4$) organic extract was evaporated to give 2-/1-(ethoxyimino)-

butyl]-3-hydroxy-5-(3-pyridyl)cyclohex-2-en-1-one as an oil.

b) <u>2-[1-(Ethoxyimino)butyl]-3-hydroxy-5-[3-(4,6-dimethyl-2-methoxypyridyl)]cyclohex-2-en-1-one</u> (20)

Ethoxyamine hydrochloride (0.21 g, 2.1 mmol) and then sodium hydroxide (84 mg, 2.1 mmol) in water (3 ml) were added to a solution of 2-butyryl-3-hydroxy-5-[3-(4,6-dimethyl-2-methoxypyridyl)]-cyclohex-2-en-1-one (0.60 g, 1.9 mmol) in ethanol (30 ml). The mixture was stirred at room temperature over night and then the ethanol was removed by evaporation under reduced pressure. The residue was dissolved in dichloromethane, washed with dilute hydrochloric acid, then water, dried over anhydrous sodium sulfate and evaporated under reduced pressure to give 2-[1-(ethoxyimino)butyl]-3-hydroxy-5-[3-(4,6-dimethyl-2-methoxypyridyl)]-cyclohex-2-en-1-one (0.57 g, 83%) as a light brown solid, mp 86-89°.

The specific Method employed for the preparation of each of the 1-[3-(substituted pyridyl)]but-1-en-3-ones of formula VIa (Example 5) and the 3-hydroxy-5-[3-(substituted pyridyl)]cyclohex-2-en-1-ones of formula IX (Example 6) and/or 2-acyl-3-hydroxy-5-[3-(substituted pyridyl)]cyclohex-2-en-1-ones of formula XIII (Example 6) used as intermediates in the preparation of the compounds of the invention of formula I are listed in Table 8 below together with the specific Method employed for the preparation of the compounds of the invention of formula I.

Each of the compounds of the invention of formula I were characterized by proton nuclear magnetic resonance spectroscopy and physical data and spectroscopic data are recorded in Example 12, Table 9.

TABLE 8

Compound No	Method of Preparation of Compounds of Formulae:		
	VIa Example 5 Method	IX and XIII Example 6 Method	I Example 7 Method
1	a	b	a
2	a	b	b
3	a	b	b
6	a	a	b
7	a	a	b
8	b	a	b
9	b	a	a
10	b	b	b
11	b	b	a
12	a	b	b
13	a	b	b
14	a	b	b
15	b	a	a
16	a	a	a
17	b	a	b
18	b	a	b
20	b	a	b
21	b	a	b
22	a	b	b
23	b	b	b
24	a	a	b
25	a	b	b
26	b	b	b
27	b	a	b
29	b	a	b
30	b	a	a

TABLE 8 continued

Compound No	Method of Preparation of Compounds of Formulae:		
	VIa Example 5 Method	IX and XIII Example 6 Method	I Example 7 Method
32	b	a	a
33	b	a	b
34	b	a	b
35	b	a	b

Example 8

2-/1-(Ethoxyimino)butyl7-3-hydroxy-5-(3-pyridyl)cyclohex-2-en-1-one methiodide (4)

a) 3-Hydroxy-5-(3-pyridyl)-2-butyrylcyclohex-2-en-1-one (1 g, 3.9 mmol) was dissolved in methyl iodide (20 ml) and the mixture was left to stand at room temperature for 12 hours. The excess methyl iodide was evaporated to give 3-hydroxy-5-(3-pyridyl)-2-butyrylcyclohex-2-en-1-one methiodide as yellow crystals, mp 162°.

Proton nuclear magnetic resonance spectrum (δ in ppm; $CDCl_3$): 0.97 (3H,t); 1.66 (2H,m); 2.89-3.9 (7H,m); 4.67 (3H,s); 8.13 (1H,s); 9.05 (1H,m); 9.56 (1H,s); 18.33 (1H,s).

b) 2-/1-(Ethoxyimino)butyl7-3-hydroxy-5-(3-pyridyl)-cyclohex-2-en-1-one methiodide was prepared from 3-hydroxy-5-(3-pyridyl)-2-butyrylcyclohex-2-en-1-one methiodide following essentially the same

procedure as that described in Example 7, Method b). The product was characterized by proton nuclear magnetic resonance spectroscopy and physical data and spectroscopic data are given in Example 12, Table 9.

Example 9

4-Ethoxycarbonyl-2-[1-(ethoxyimino)butyl]-3-hydroxy-5-(3-pyridyl)cyclohex-2-en-1-one (5)

a) 2-Butyryl-4-ethoxycarbonyl-3-hydroxy-5-(3-pyridyl)-cyclohex-2-en-1-one was isolated as a minor faster-moving component on purification of 2-butyryl-3-hydroxy-5-(3-pyridyl)cyclohex-2-en-1-one (Example 6, Method b) by column chromatography. The product was obtained as a yellow oil and was characterized by proton nuclear magnetic resonance spectroscopy. Pmr spectrum (δ in ppm; $CDCl_3$): 0.93-1.17 (6H,m); 1.72 (2H,m); 2.86-3.86 (6H,m); 4.06 (2H,m); 7.3-8.8 (4H,m); OH not observed.

b) 4-Ethoxycarbonyl-2-[1-(ethoxyimino)butyl]-3-hydroxy-5-(3-pyridyl)cyclohex-2-en-1-one was prepared from 2-butyryl-4-ethoxycarbonyl-3-hydroxy-5-(3-pyridyl)cyclohex-2-en-1-one following essentially the same procedure as that described in Example 7, Method b). The product was characterized by proton nuclear magnetic resonance spectroscopy and physical data and spectroscopic data are given in Example 12, Table 9.

Example 10

Sodium salt of 2-[1-(ethoxyimino)propyl]-3-hydroxy-5-[3-(4,6-dimethyl-2-methoxypyridyl)]cyclohex-2-en-1-one (19) and sodium salt of 2-[1-(ethoxyimino)butyl]-3-hydroxy-5-[3-(5-chloro-4,6-dimethyl-2-methoxypyridyl)]cyclohex-2-en-1-one (28)

a) 2-[1-(Ethoxyimino)propyl]-3-hydroxy-5-[3-(4,6-dimethyl-2-methoxypyridyl)]cyclohex-2-en-1-one (1.0 g, 2.89 mmol) and sodium hydroxide (116 mg, 2.89 mmol) were stirred in acetone (50 ml) at room temperature for 2 hours. The solvent was evaporated and the residue was suspended in toluene (50 ml). Evaporation of the solvent gave the sodium salt of 2-[1-(ethoxyimino)propyl]-3-hydroxy-5-[3-(4,6-dimethyl-2-methoxypyridyl)]-cyclohex-2-en-1-one, mp >250^{o} (dec.).

b) The sodium salt of 2-[1-(ethoxyimino)butyl]-3-hydroxy-5-[3-(5-chloro-4,6-dimethyl-2-methoxypyridyl)]cyclohex-2-en-1-one was prepared from 2-[1-(ethoxyimino)butyl]-3-hydroxy-5-[3-(5-chloro-4,6-dimethyl-2-methoxypyridyl)]cyclohex-2-en-1-one following essentially the same procedure as that described above. The product was obtained as a pale yellow solid, mp >250^{o}C.

Example 11

2-[1-(Ethoxyimino)butyl]-5-[3-(2-chloro-4,5,6-trimethylpyridyl)]-3-(3-methylbutanoyl)cyclohex-2-en-1-one (31)

3-Methylbutanoyl chloride (0.17 g) and 4-methylpyridine (0.14 g) were added dropwise to a solution of 2-[1-(ethoxyimino)butyl]-5-[3-(2-chloro-4,5,6-trimethyl-

pyridyl)]cyclohex-2-en-1-one (0.5 g) in dichloromethane (40 ml) and the mixture was stirred at room temperature for 1 hour. The solvent was evaporated and the residue was purified by column chromatography over silica gel with dichloromethane/methanol elution to give 2-[1-(ethoxyimino)butyl]-5-[3-(2-chloro-4,5,6-trimethylpyridyl)]-3-(3-methylbutanoyl)cyclohex-2-en-1-one (0.5 g, 83%). The product was characterized by proton nuclear magnetic resonance spectroscopy and appropriate physical data are recorded in Example 12 Table 9).

Example 12

The compounds of the invention of formula I were characterized by and may be identified by their proton nuclear magnetic resonance spectra. For convenience physical data and pmr spectroscopic data for the compounds of the invention of formula I are recorded in Table 9 below.

TABLE 9

Compound No	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
1	Oil	0.99(3H,t); 1.33(3H,t); 1.59(2H, m); 2.71-3.6(7H,m); 4.12(2H,q); 7.3-8.54(4H,m); 10.6(1H,s).
2	Oil	0.98(3H,t); 1.59(2H,m); 2.68-3.6(7H,m); 4.55(2H,d); 5.27-8.6 (7H,m).

TABLE 9 continued

Compound No	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
3	Brown oil	0.98(3H,t); 1.26-1.72(2H,m); 2.58-3.10(4H,m); 3.32-3.85(3H,m); 4.65(2H,dofd); 5.74-6.42 (2H,m); 7.34-8.32(4H,m); 10.85 (1H,brs).
4	Yellow solid, mp 143^{o} (dec)	0.95(3H,s); 1.32(3H,s); 1.55(2H,m); 2.81-3.8(7H,m); 4.1(2H,q); 4.65(3H,s); 8.16(1H,m); 8.51 (1H,m); 9.12(1H,m); 9.46(1H,s).
5	Yellow oil	0.92-1.14(6H,m); 1.34(3H,t); 1.6(2H,m); 2.74-3.76(6H,m); 3.95-4.24(4H,m); 7.3-8.6(4H,m); OH not observed.
6	White solid, mp 78^{o}	0.99(3H,t); 1.33(3H,t); 1.41-1.68(2H,m); 2.55(3H,s); 2.64-3.04(6H,m); 3.12-3.44(1H,m); 4.11(2H,q); 7.12(1H,d); 7.46 (1H,m); 8.4(1H,d); 15.24(1H,brs).
7	White solid, mp 82^{o}	0.99(3H,t); 1.33(3H,t); 1.47-2.43(2H,m); 2.51(3H,s); 2.64-3.05(6H,m); 3.13-3.75(1H,m); 4.12(2H,q); 7.10 (1H,d); 7.48 (1H,d); 15.29(1H,brs).
8	White solid, mp 86^{o}	0.97(3H,t); 1.31(3H,t); 1.57 (2H,m); 2.41(3H,s); 2.4-3.9 (5H,m); 3.94(3H,s); 4.1(2H,q); 6.67(2H,d); 7.25(2H,d); 15.08 (1H,s).

TABLE 9 continued

Compound No	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
9	White solid, mp 76-78°	0.98(3H,t); 1.33(3H,t); 1.59 (2H,m); 3.78(3H,s); 3.88(3H,s); 3.90(3H,s); 2.13-4.38(9H,m); 5.88(1H,s); 14.58(1H,brs).
10	White solid, mp 118°	0.97(3H,t); 1.33(3H,t); 1.43-1.78(2H,m); 2.41(3H,s); 2.52 (2H,brs); 2.94(2H,t); 3.15-3.93(3H,m); 4.12(2H,q); 7.12 (1H,s); 15.36(1H,s).
11	Not recorded	1.00(3H,t); 1.2-4.28(15H,m); 2.26(3H,s); 3.88(3H,s); 3.97 (3H,s); 6.17(1H,s).
12	Yellow oil	1.01(3H,t); 1.34(3H,t); 1.43-1.89(2H,m); 2.37-2.63(5H,m); 2.96(2H,t); 3.51(2H,t); 4.02-4.49(3H,m); 7.18(1H,s); 14.5-15.0(1H,brs).
13	Oil	1.00(3H,t); 1.35(3H,t); 1.59 (2H,m); 2.4-4.0(7H,m); 2.61(3H, s); 4.15(2H,q); 7.42(1H,s); 14.89(1H,s).
14	Oil	1.00(3H,t); 1.32(3H,t); 1.62(2H, m); 2.48(3H,s); 2.40-4.00(7H, m); 3.99(3H,s); 4.11(2H,q); 6.98 (1H,s); 15.14(1H,s).

TABLE 9 continued

Compound No	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
15	Oil	1.00(3H,t); 1.33(3H,t); 1.46-1.73(2H,m); 2.27-4.90(9H,m); 2.45(3H,s); 2.67(3H,s); 7.01 (1H,s); 15.32(1H,brs).
16	Yellow-brown oil	1.00(3H,t); 1.34(3H,t); 1.43-1.81(2H,m); 2.38(3H,s); 2.39 (3H,s); 2.57(2H,m); 2.70-3.04 (2H,t); 3.16-3.90(3H,m); 4.13 (2H,q); 14.69(1H,s).
17	Oil	1.00(3H,t); 1.33(3H,t); 1.56 (2H,m); 2.40(3H,s); 2.45(3H,s); 2.40-3.95(5H,m); 4.13(2H,q); 6.94(1H,s); 14.36(1H,s).
18	White solid	1.20(3H,t); 1.33(3H,t); 2.26 (3H,s); 2.36(3H,s); 2.30-3.90 (5H,m); 2.95(2H,q); 3.92(3H,s); 4.12(2H,q); 6.55(1H,s); 14.77 (1H,s).
20	Light brown solid, mp 86-89°	1.0(3H,t); 1.32(3H,t); 1.61 (2H,q); 2.26(3H,s); 2.36(3H,s); 2.2-2.6 (2H,m); 2.7-3.8(5H,m); 3.92(3H,s); 4.11(2H,q); 6.55 (1H,s); 15.2(1H,s).
21	Not recorded	1.00(3H,t); 1.23-1.46(6H,2xt); 1.64(2H,m); 2.24(3H,s); 2.34(3H,s); 2.3-3.9(7H,m); 4.11(2H,q); 4.39(2H,q); 6.53(1H,s); 15.07 (1H,s).

TABLE 9 continued

Compound No	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
22	Oil	1.00(3H,t); 1.32(3H,t); 1.45-1.70(2H,m); 2.10-4.23(9H,m); 2.31(3H,s); 2.42(3H,s); 2.57(3H,s); 6.66(1H,s); 15.11(1H,brs).
23	Colourless oil	1.00(3H,t); 1.34(3H,t); 1.61(2H,m); 2.61(6H,s); 2.92(2H,m); 2.26-3.95(5H,m); 4.13(2H,q); 15.17(1H,brs).
24	Pale yellow solid, mp 123-24°	1.13-1.42(6H,m); 2.41-4.26(9H,m); 2.41(3H,s); 2.52(3H,s); 15.0-15.5(1H,brs).
25	Yellow solid	1.00(3H,t); 1.33(3H,t); 1.42-1.70(2H,m); 2.30-4.24(9H,m); 2.50(3H,s); 2.58(3H,s); 15.31(1H,s).
26	Cream solid, mp 98°	1.00(3H,t); 1.34(3H,t); 1.45-1.74(2H,m); 2.32-3.02(2H,m); 2.56(3H,s); 2.64(3H,s); 3.32-3.84(5H,m); 4.13(2H,q); 15.22(1H,s).
27	Oil	1.00(3H,t); 1.33(3H,t); 1.48-1.68(2H,m); 2.20-4.15(9H,m); 2.38(3H,s); 2.49(3H,s); 3.92(3H,s); 15.13(1H,brs).

TABLE 9 continued

Compound No	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
29	Oil	1.00(3H,t); 1.33(3H,t); 1.61 (2H,m); 2.37(3H,s); 2.44(3H,s); 2.60(3H,s); 4.09(2H,q); 2.12-4.30(7H,m); 6.80(1H,s); 12.70 (1H,brs).
30	White solid, mp 77°	1.00(3H,t); 1.33(3H,t); 1.60(2H, m); 2.21(3H,s); 2.33(3H,s); 2.47(3H,s); 2.41-3.96(7H,m); 4.13(2H,q); 15.06(1H,brs).
31	Pale yellow oil	0.74-1.06(9H,m); 1.08-1.71(6H, m); 2.00-2.71(6H,m); 2.22(3H, s); 2.36(3H,s); 2.50(3H,s); 3.26-4.34(5H,m).
32	White solid, mp 94°	1.00(3H,t); 1.33(3H,t); 1.60 (2H,m); 2.13(3H,s); 2.22(3H,s); 2.40(3H,s); 3.90(3H,s); 2.41-3.96(7H,m); 4.11(2H,q); 14.95 (1H,brs).
33	Cream low-melting solid	1.00(3H,t); 1.38-1.81(2H,m); 2.16(3H,s); 2.24(3H,s); 2.41 (3H,s); 2.58(1H,m); 2.87(2H,t); 3.15-3.79(5H,m); 3.90(3H,s); 4.64(1H,s); 4.66(1H,s); 13.93 (1H,s).

TABLE 9 continued

Compound No	Appearance	Proton Chemical Shift δ in ppm ($CDCl_3$)
34	Colourless oil	0.99(3H,t); 1.43-1.84(2H,m); 2.14(3H,s); 2.22(3H,s); 2.41 (3H,s); 2.90(2H,t); 3.10-3.70 (5H,m); 3.90(3H,s); 4.02-4.25 (1H,m); 4.30-4.53(2H,m); 4.81-4.99(1H,m); 14.09(1H,s).
35	Pale yellow oil	1.00(3H,t); 1.43-1.72(2H,m); 2.14(3H,s); 2.21(3H,s); 2.40 (3H,s); 2.87(2H,t); 3.16-3.73 (5H,m); 3.90(3H,s); 4.71(2H, dofd); 5.85-6.49(2H,m); 14.27 (1H,s).

Example 13

This non-limiting Example illustrates the preparation of formulations of the compounds of the invention.

a) Emulsifiable Concentrate

Compound No 25 was dissolved in toluene containing 7% v/v "Teric" N13 and 3% v/v "Kemmat" SC15B to give an emulsifiable concentrate which may be diluted with water to the required concentration to give an aqueous emulsion which may be applied by spraying.

("Teric" is a Trade Mark and "Teric" N13, is a product of ethoxylation of nonylphenol; "Kemmat" is a Trade Mark and "Kemmat" SC15B is a formulation of calcium dodecylbenzenesulfonate.)

b) Aqueous Suspension

Compound No 25 (5 parts by weight) and "Dyapol" PT (1 part by weight) were added to an aqueous solution (94 parts by weight) of "Teric" N8 and the mixture was ball milled to produce a stable aqueous suspension which may be diluted with water to the required concentration to give an aqueous suspension which may be applied by spraying. ("Dyapol" is a Trade Mark and "Dyapol" PT is an anionic suspending agent; "Teric" N8 is a product of ethoxylation of nonylphenol.)

c) Emulsifiable Concentrate

Compound No 25 (10 parts by weight), "Teric" N13 (5 parts by weight) and "Kemmat" SC15B (5 parts by weight) were dissolved in "Solvesso" 150 (80 parts by weight) to give an emulsifiable concentrate which may be diluted with water to the required concentration to give an aqueous emulsion which may be applied by spraying. ("Solvesso" is a Trade Mark and "Solvesso" 150 is a high boiling point aromatic petroleum fraction.)

d) Dispersible Powder

Compound No 25 (10 parts by weight), "Matexil" DA/AC (3 parts by weight), "Aerosol" OT/B (1 part by weight) and china clay 298 (86 parts by weight) were blended and then milled to give a powder composition having a particle size below 50 microns.

("Matexil" is a Trade Mark and "Matexil" DA/AC is the disodium salt of a naphthalenesulfonic acid/ formaldehyde condensate; "Aerosol" is a Trade Mark and "Aerosol" OT/B is a formulation of the dioctyl ester of sodium sulfosuccinic acid.)

e) High Strength Concentrate

Compound No 25 (99 parts by weight), silica aerogel (0.5 parts by weight) and synthetic amorphous silica (0.5 parts by weight) were blended and ground in a hammer-mill to produce a powder having a particle size less than 200 microns.

f) Dusting Powder

Compound No 25 (10 parts by weight), attapulgite (10 parts by weight) and pyrophyllite (80 parts by weight) were thoroughly blended and then ground in a hammer-mill to produce a powder of particle size less than 200 microns.

Emulsifiable concentrates and/or suspensions of the compounds of the invention were prepared essentially as described in part a), b) or c) above and then diluted with water, optionally containing surface active agent and/or oil, to give aqueous compositions of the required concentration which were used, as described in Examples 14 and 15, in the evaluation of the pre-emergence and post-emergence herbicidal activity of the compounds.

Example 14

The pre-emergent herbicidal activity of the compounds of the invention formulated as described in Example 13 was assessed by the following procedure:

The seeds of the test species were sown in rows 2 cm deep in soil contained in seed boxes. The monocotyledonous plants and dicotyledonous plants were sown in separate boxes and after sowing the two boxes were sprayed with the required quantity of a composition of the invention. Two duplicate seed boxes were prepared in the same manner but were not sprayed with a composition of the invention and were used for comparison purposes. All the boxes were placed in a glasshouse, lightly watered with an overhead spray to initiate germination and then sub-irrigated as required for optimum plant growth. After three weeks the boxes were removed from the glass house and the effect of the treatment was visually assessed. The results are presented in Table 10 where the damage to plants is rated on a scale of from 0 to 5 where 0 represents from 0 to 10% damage, 1 represents from 11 to 30% damage, 2 represents from 31 to 60% damage, 3 represents from 61 to 80% damage, 4 represents from 81 to 99% damage and 5 represents 100% kill. A dash (-) means that no experiment was carried out.

The names of the test plants are as follows:

Wh	Wheat
Ot	Wild Oats
Rg	Ryegrass
Jm	Japanese millet
P	Peas
Ip	Iponea
Ms	Mustard
Sf	Sunflower

TABLE 10

PRE-EMERGENCE HERBICIDAL ACTIVITY

Compound No	APPLICATION Rate (kg/ha)	TEST PLANT							
		Wh	Ot	Rg	Jm	P	Ip	Ms	Sf
1	1.0	1	0	3	1	0	0	0	0
2	1.0	4	4	4	4	0	0	0	0
4	1.0	0	0	0	0	0	0	0	0
5	1.0	0	0	0	0	0	0	0	0
6	1.0	0	0	5	4	0	0	0	0
7	1.0	0	0	1	3	0	0	0	0
8	1.0	0	0	5	5	0	0	0	0
9	1.0	0	0	4	3	0	0	0	0
10	0.25	0	1	4	3	0	0	0	0
11	1.0	0	0	0	5	0	0	0	0
12	0.9	4	5	5	5	0	0	0	0
12	0.25	2	2	5	5	0	0	0	0
13	0.25	0	3	5	5	0	0	0	0
15	1.0	0	4	5	5	0	0	0	0
16	1.0	0	3	5	5	0	0	0	0
17	1.0	5	5	5	5	0	0	0	0
17	0.25	3	4	5	5	0	0	0	0
18	1.0	0	3	4	0	0	0	0	0
19	1.0	0	4	4	0	0	0	0	0
20	0.25	1	5	5	5	0	0	0	0
20	0.0625	0	3	5	5	0	0	0	0
21	1.0	0	5	4	5	0	0	0	0
21	0.25	0	3	3	5	0	0	0	0
22	1.0	5	5	4	5	0	0	0	0
22	0.25	3	4	5	5	0	0	0	0

TABLE 10 continued

Compound No	APPLICATION Rate (kg/ha)	TEST PLANT							
		Wh	Ot	Rg	Jm	P	Ip	Ms	Sf
23	1.0	0	5	5	5	0	0	0	0
23	0.25	0	3	4	4	0	0	0	0
24	1.0	5	5	5	5	0	0	0	0
24	0.25	0	1	5	5	0	0	0	0
25	1.0	0	0	5	3	0	0	0	0
28	1.0	0	4	2	3	0	0	0	0
30	1.0	4	5	4	5	0	0	0	0
30	0.25	1	4	5	5	0	0	0	0
31	1.0	0	5	5	5	0	0	0	0
31	0.25	0	2	4	4	0	0	0	0
32	1.0	4	4	5	5	0	0	0	0
32	0.25	3	4	5	5	0	0	0	0

Example 15

The post-emergent herbicidal activity of the compounds of the invention formulated as described in Example 13 was assessed by the following procedure.

The seeds of the test species were sown in rows 2 cm deep in soil contained in seed boxes. The monocotyledonous plants and the dicotyledonous plants were sown in separate seed boxes in duplicate. The four seed boxes were placed in a glass house, lightly watered with an overhead spray to initiate germination and then sub-irrigated as required for optimum plant growth. After the plants had grown to a height of about 10 to 12.5 cm one box of each of the mono-

cotyledonous plants and the dicotyledonous plants was removed from the glass house and sprayed with the required quantity of a composition of the invention. After spraying the boxes were returned to the glass house for a further 3 weeks and the effect of treatment was visually assessed by comparison with the untreated controls. The results are presented in Table 11 where the damage to plants is rated on a scale of from 0 to 5 where 0 represents from 0 to 10% damage, 1 represents from 11 to 30% damage, 2 represents from 31 to 60% damage, 3 represents from 61 to 80% damage, 4 represents from 81 to 99% damage and 5 represents 100% kill. A dash (-) means that no experiment was carried out.

The names of the test plants are as follows:

Wh	Wheat
Ot	Wild Oats
Rg	Ryegrass
Jm	Japanese millet
P	Peas
Ip	Ipomea
Ms	Mustard
Sf	Sunflower

TABLE 11

POST-EMERGENCE HERBICIDAL ACTIVITY

Compound No	APPLICATION Rate (kg/ha)	TEST PLANT							
		Wh	Ot	Rg	Jm	P	Ip	Ms	Sf
1	1.0	5	5	5	5	0	0	0	0
1	0.25	1	4	5	5	0	0	0	0
2	1.0	5	5	5	5	0	0	0	0
2	0.25	3	5	3	5	0	0	0	0
4	1.0	0	0	0	0	0	0	0	0
5	1.0	0	0	0	0	0	0	0	0
6	1.0	3	4	5	5	0	0	0	0
6	0.25	2	4	5	5	0	0	0	0
7	1.0	0	5	5	5	0	0	0	0
7	0.25	0	0	4	5	0	0	0	0
8	1.0	0	0	4	5	0	0	0	0
8	0.25	0	0	3	4	0	0	0	0
9	1.0	0	5	5	5	0	0	0	0
9	0.25	0	4	4	4	0	0	0	0
9	0.0625	0	3	2	3	0	0	0	0
10	0.25	3	3	5	5	0	0	0	0
10	0.0625	0	2	4	3	0	0	0	0
11	1.0	0	5	5	5	0	0	0	0
11	0.25	0	4	3	5	0	0	0	0
11	0.0625	0	0	2	5	0	0	0	0
12	0.9	5	5	5	5	0	0	0	0
12	0.25	5	5	5	5	0	0	0	0
12	0.0625	1	5	5	5	0	0	0	0

TABLE 11 continued

Compound No	APPLICATION Rate (kg/ha)	TEST PLANT							
		Wh	Ot	Rg	Jm	P	Ip	Ms	Sf
13	0.25	3	5	5	5	0	0	0	0
13	0.0625	2	4	4	5	0	0	0	0
15	1.0	5	5	4	5	0	0	0	0
15	0.25	2	5	4	5	0	0	0	0
15	0.0625	1	5	5	5	0	0	0	0
16	1.0	4	5	5	5	0	0	0	0
16	0.25	2	4	4	5	0	0	0	0
16	0.0625	0	4	3	4	0	0	0	0
17	1.0	5	5	5	5	0	0	0	0
17	0.25	1	5	5	5	0	0	0	0
17	0.0625	0	5	4	5	0	0	0	0
18	1.0	5	5	5	5	0	0	0	0
18	0.25	5	5	5	5	0	0	0	0
18	0.0625	1	5	5	5	0	0	0	0
19	1.0	5	5	5	5	0	0	0	0
19	0.25	2	5	4	5	0	0	0	0
19	0.0625	0	2	2	4	0	0	0	0
20	1.0	5	5	5	5	0	0	0	0
20	0.25	5	5	5	5	0	0	0	0
20	0.0625	1	5	5	5	0	0	0	0
21	1.0	5	5	5	5	0	0	0	0
21	0.25	1	5	4	5	0	0	0	0
21	0.0625	0	5	4	5	0	0	0	0
22	1.0	5	5	4	5	0	0	0	0
22	0.25	4	5	5	5	0	0	0	0
22	0.0625	2	5	5	4	0	0	0	0

TABLE 11 continued

Compound No	APPLICATION Rate (kg/ha)	TEST PLANT							
		Wh	Ot	Rg	Jm	P	Ip	Ms	Sf
23	1.0	5	5	5	5	0	0	0	0
23	0.25	1	5	5	5	0	0	0	0
23	0.0625	0	5	5	5	0	0	0	0
24	1.0	5	5	5	5	0	0	0	0
24	0.25	4	5	5	5	0	0	0	0
24	0.0625	0	4	5	5	0	0	0	0
25	1.0	2	5	5	5	0	0	0	0
25	0.25	1	5	5	5	0	0	0	0
25	0.0625	0	5	5	5	0	0	0	0
27	1.0	5	5	5	5	0	0	0	0
27	0.25	1	5	5	5	0	0	0	0
27	0.0625	0	5	4	3	0	0	0	0
30	1.0	5	5	5	5	0	0	0	0
30	0.25	0	5	5	5	0	0	0	0
30	0.0625	0	5	5	5	0	0	0	0
31	1.0	4	5	5	5	0	0	0	0
31	0.25	0	5	4	5	0	0	0	0
31	0.0625	0	5	4	5	0	0	0	0
32	1.0	5	5	5	5	0	0	0	0
32	0.25	5	5	5	5	0	0	0	0
32	0.0625	4	5	5	5	0	0	0	0

Example 16

The compounds were formulated for test by mixing an appropriate amount with 5 ml of an emulsion prepared by diluting 160 ml of a solution containing 21.9 g per litre of "Span" 80 and 78.2 g per litre of "Tween" 20 in methylcyclohexanone to 500 ml with water. "Span" 80 is a Trade Mark for a surface-active agent comprising sorbitan monolaurate. "Tween" 20 is a Trade mark for a surface-active agent comprising a condensate of sorbitan monolaurate with 20 molar proportions of ethylene oxide. Each 5 ml emulsion containing a test compound was then diluted to 40 ml with water and sprayed on to young pot plants (post-emergence test) of the species named in Table 12 below. Damage to test plants was assessed after 14 days on a scale of 0 to 5 where 0 is 0 to 20% damage and 5 is complete kill In a test for pre-emergence herbicidal activity, seeds of the test plants were sown in a shallow slit formed in the surface of soil in fibre trays. The surface was then levelled and sprayed, and fresh soil then spread thinly over the sprayed surface. Assessment of herbicidal damage was carried out after 21 days using the same scale of 0 to 5 as the post-emergence test. In both cases the degree of herbicidal damage was assessed by comparison with untreated control plants. The results are given in Table 12 below. A dash (-) means that no experiment was carried out.

The names of the test plants were as follows:

Sb	Sugar beet
Rp	Rape
Ct	Cotton
Sy	Soy bean
Mz	Maize
Ww	Winter wheat

Rc	Rice
Sn	Senecio vulgaris
Ip	Ipomea purpurea
Am	Amaranthus retroflexus
Pi	Polygonum aviculare
Ca	Chenopodium album
Ga	Galium aparine
Xa	Xanthium pensylvanicum
Ab	Abutilon theophrasti
Co	Cassia obtusifolia
Av	Avena fatua
Dg	Digitaria sanguinalis
Al	Alopecurus myosuroides
St	Setaria viridis
Ec	Echinochloa crus-galli
Sh	Sorghum halepense
Ag	Agropyron repens
Cn	Cyperus rotundas

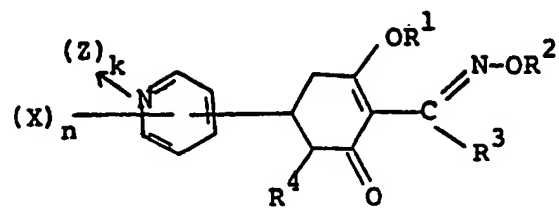
TABLE 12 - PART A

Compound No	APPLICATION Method	Rate (kg/ha)	TEST PLANT Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi
8	PRE	0.4	-	-	-	-	-	0	-	-	-	-	-
8	POST	2.0	-	-	-	-	-	2	-	-	-	-	-
8	POST	0.2	-	-	-	-	4	0	2	-	-	-	-
8	POST	0.05	-	-	-	-	3	0	1	-	-	-	-
17	PRE	0.2	-	-	-	-	-	4	-	-	-	-	-
17	POST	1.0	-	-	-	-	-	4	-	-	-	-	-
17	POST	0.2	-	-	-	-	-	4	-	-	-	-	-
17	POST	0.05	-	-	-	-	-	1	-	-	-	-	-
20	PRE	0.4	-	-	-	-	-	5	-	-	-	-	-
20	PRE	0.2	-	-	-	-	5	5	5	-	-	-	-
20	PRE	0.05	-	-	-	-	5	3	5	-	-	-	-
20	POST	0.2	-	-	-	-	5	4	4	-	-	-	-
20	POST	0.05	-	-	-	-	4	0	4	-	-	-	-
20	POST	0.02	-	-	-	-	3	0	2	-	-	-	-
20	POST	0.01	-	-	-	-	2	1	0	-	-	-	-
21	PRE	0.2	-	-	-	-	4	5	5	-	-	-	-
21	PRE	0.05	-	-	-	-	2	1	4	-	-	-	-
21	POST	0.2	-	-	-	-	5	3	3	-	-	-	-
21	POST	0.05	-	-	-	-	4	0	5	-	-	-	-
27	PRE	0.2	-	-	-	-	-	2	-	-	-	-	-
27	POST	1.0	-	-	-	-	-	4	-	-	-	-	-
27	POST	0.2	-	-	-	-	-	3	-	-	-	-	-
27	POST	0.05	-	-	-	-	-	0	-	-	-	-	-
32	POST	0.4	-	-	-	-	5	4	4	-	-	-	-
32	POST	0.1	-	-	-	-	5	0	2	-	-	-	-
32	POST	0.02	-	-	-	-	1	0	0	-	-	-	-

TABLE 12 - PART B

Compound No	APPLICATION Method	Rate (kg/ha)	Ga	Xa	Ab	Co	Av	Dg	Al	St	Ec	Sh	Ag
8	PRE	0.4	-	-	-	-	1	-	4	-	-	-	-
8	POST	2.0	-	-	-	-	4	-	-	-	-	-	-
8	POST	0.2	-	-	-	-	2	4	1	4	4	4	0
8	POST	0.05	-	-	-	-	0	4	-	3	4	1	-
17	PRE	0.2	-	-	-	-	5	-	5	-	-	-	-
17	POST	1.0	-	-	-	-	5	-	-	-	-	-	-
17	POST	0.2	-	-	-	-	5	-	-	-	-	-	-
17	POST	0.05	-	-	-	-	4	-	-	-	-	-	-
20	PRE	0.4	-	-	-	-	5	-	5	-	-	-	-
20	PRE	0.2	-	-	-	-	5	5	5	5	5	5	5
20	PRE	0.05	-	-	-	-	5	3	5	5	5	4	5
20	POST	0.2	-	-	-	-	5	4	4	5	5	4	3
20	POST	0.05	-	-	-	-	4	4	3	4	4	4	1
20	POST	0.02	-	-	-	-	4	2	3	4	4	3	0
20	POST	0.01	-	-	-	-	0	1	1	3	3	2	0
21	PRE	0.2	-	-	-	-	5	4	5	3	5	4	5
21	PRE	0.05	-	-	-	-	5	3	4	1	1	2	1
21	POST	0.2	-	-	-	-	5	5	4	5	5	4	3
21	POST	0.05	-	-	-	-	4	5	4	4	4	4	1
27	PRE	0.2	-	-	-	-	5	-	5	-	-	-	-
27	POST	1.0	-	-	-	-	5	-	-	-	-	-	-
27	POST	0.2	-	-	-	-	5	-	-	-	-	-	-
27	POST	0.05	-	-	-	-	4	-	-	-	-	-	-
32	POST	0.4	-	-	-	-	5	5	5	5	5	5	5
32	POST	0.1	-	-	-	-	5	5	5	5	5	5	4
32	POST	0.02	-	-	-	-	2	4	4	2	4	4	1

1. A compound of formula I or an isomer thereof



I

wherein:

Z is selected from oxygen and the group -YAn wherein Y is selected from C_1 to C_6 alkyl and benzyl and An is an anion selected from halide, tetrafluoroborate, methosulfate and fluorosulfate;

X, which may be the same or different, are independently selected from the group consisting of: halogen, nitro; cyano; C_1 to C_6 alkyl; C_1 to C_6 alkyl substituted with a substituent selected from the group consisting of halogen, nitro, hydroxy, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; hydroxy; C_1 to C_6 alkoxy; C_1 to C_6 alkoxy substituted with a substituent selected from halogen and C_1 to C_6 alkoxy; C_2 to C_6 alkenyloxy; C_2 to C_6 alkynyloxy; C_2 to C_6 alkanoyloxy; (C_1 to C_6 alkoxy)carbonyl; C_1 to C_6 alkylthio; C_1 to C_6 alkylsulfinyl; C_1 to C_6 alkylsulfonyl; sulfamoyl; N-(C_1 to C_6 alkyl)sulfamoyl; N,N-di(C_1 to C_6 alkyl)sulfamoyl; benzyloxy; substituted benzyloxy wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, C_1 to C_6 alkyl, C_1 to C_6 alkoxy and C_1 to C_6 haloalkyl; the group NR^5R^6 wherein R^5 and R^6 are independently selected from the group consisting of hydrogen, C_1 to C_6 alkyl, C_2 to C_6 alkanoyl, benzoyl and benzyl; the groups formyl and C_2 to C_6 alkanoyl and the oxime, imine and Schiff base derivatives there-

of;

R^1 is selected from the group consisting of: hydrogen; C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_1 to C_6 alkylsulfonyl; benzenesulfonyl; substituted benzenesulfonyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; an acyl group; and an inorganic or organic cation;

R^2 is selected from the group consiting of: C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 haloalkenyl; C_2 to C_6 alkynyl; C_2 to C_6 haloalkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of halogen, C_1 to C_6 alkoxy, C_1 to C_6 alkylthio; phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio;

R^3 is selected from the group consisting of: C_1 to C_6 alkyl; C_1 to C_6 fluoroalkyl; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; and phenyl;

R^4 is selected from the group consisting of: hydrogen; halogen; cyano; C_1 to C_6 alkyl; and (C_1 to C_6 alkoxy)-

carbonyl;

k is zero or the integer 1; and

n is zero or an integer selected from 1 to 4.

2. A compound according to claim 1 wherein:

Z is selected from oxygen and the group -YAn wherein Y is selected from C_1 to C_6 alkyl and benzyl and An is an anion selected from halide, tetrafluoroborate, methosulfate and fluorosulfate;

X, which may be the same or different, are independently selected from the group consisting of: halogen, nitro; cyano; C_1 to C_6 alkyl; C_1 to C_6 alkyl substituted with a substituent selected from the group consisting of halogen, nitro, hydroxy, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; hydroxy; C_1 to C_6 alkoxy; C_1 to C_6 alkoxy substituted with a substituent selected from halogen and C_1 to C_6 alkoxy; C_2 to C_6 alkenyloxy; C_2 to C_6 alkynyloxy; C_2 to C_6 alkanoyloxy; (C_1 to C_6 alkoxy)carbonyl; C_1 to C_6 alkylthio; C_1 to C_6 alkylsulfinyl; C_1 to C_6 alkylsulfonyl; sulfamoyl; N-(C_1 to C_6 alkyl)sulfamoyl; N,N-di(C_1 to C_6 alkyl)sulfamoyl; benzyloxy; substituted benzyloxy wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, C_1 to C_6 alkyl, C_1 to C_6 alkoxy and C_1 to C_6 haloalkyl; the group NR^5R^6 wherein R^5 and R^6 are independently selected from the group consisting of hydrogen, C_1 to C_6 alkyl, C_2 to C_6 alkanoyl, benzoyl and benzyl; and the group of the formula $-C(R^7)=NR^8$ wherein R^7 is chosen from hydrogen and C_1 to C_5 alkyl, and R^8 is chosen from hydrogen, C_1 to C_6 alkyl, phenyl, benzyl, hydroxy, C_1 to C_6 alkoxy, phenoxy and benzyloxy;

R^1 is selected from the group consisting of: hydrogen; C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_1 to C_6 alkylsulfonyl; benzenesulfonyl; substituted benzenesulfonyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_2 to C_6 alkanoyl; benzoyl; substituted benzoyl wherein the benzene ring is substituted with from one to three substituents chosen from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; 2-furoyl; 3-furoyl; 2-thenoyl; 3-thenoyl; and an organic or inorganic cation selected from the alkali metal ions, the alkaline earth metal ions, the transition metal ions and the ammonium ion $R^9R^{10}R^{11}R^{12}N^{\oplus}$ wherein R^9, R^{10}, R^{11} and R^{12} are independently selected from the group consisting of: hydrogen; C_1 to C_{10} alkyl; substituted C_1 to C_{10} alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of hydroxy, halogen and C_1 to C_6 alkoxy; phenyl; benzyl; and the groups substituted phenyl and substituted benzyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio;

R^2 is selected from the group consisting of: C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 haloalkenyl; C_2 to C_6 alkynyl; C_2 to C_6 haloalkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of halogen, C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio;

R^3 is selected from the group consisting of: C_1 to C_6 alkyl; C_1 to C_6 fluoroalkyl; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; and phenyl;

R^4 is selected from the group consisting of: hydrogen; halogen; cyano; C_1 to C_6 alkyl; and (C_1 to C_6 alkoxy)-carbonyl;

k is zero or the integer 1; and

n is zero or an integer selected from 1 to 4.

3. A compound according to claim 1 or claim 2 wherein:

Z is oxygen;

X is selected from the group consisting of: halogen; nitro; cyano; C_1 to C_6 alkyl; C_1 to C_6 alkyl substituted with halogen, nitro or C_1 to C_6 alkoxy; C_1 to C_6 alkoxy; C_1 to C_6 alkoxy substituted with halogen or C_1 to C_6 alkoxy; C_2 to C_6 alkanoyloxy; (C_1 to C_6 alkoxy)-carbonyl; C_1 to C_6 alkylthio; C_1 to C_6 alkylsulfinyl; C_1 to C_6 alkylsulfonyl; sulfamoyl; N-(C_1 to C_6 alkyl)-sulfamoyl; N,N-di(C_1 to C_6 alkyl)sulfamoyl; benzyloxy; substituted benzyloxy wherein the benzene ring is sub-

stituted with from one to three substituents selected from the group consisting of halogen, nitro, C_1 to C_6 alkyl, C_1 to C_6 alkoxy and C_1 to C_6 haloalkyl; the group NR^5R^6 wherein R^5 and R^6 are independently selected from hydrogen, C_1 to C_6 alkyl, C_2 to C_6 alkanoyl, benzoyl and benzyl; and a group of the formula $-C(R^7)=NR^8$ wherein R^7 is selected from hydrogen and C_1 to C_5 alkyl and R^8 is selected from hydrogen, C_1 to C_6 alkyl, phenyl, benzyl, hydroxy, C_1 to C_6 alkoxy, phenoxy and benzyloxy;

R^1 is selected from the group consisting of: hydrogen; C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 alkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_1 to C_6 alkylsulfonyl; benzenesulfonyl; substituted benzenesulfonyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; C_2 to C_6 alkanoyl; benzoyl; substituted benzoyl wherein the benzene ring is substituted with from one to three substituents chosen from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio; 2-furoyl; 3-furoyl; 2-thenoyl; 3-thenoyl; and an organic or inorganic cation selected from the alkali metal ions, the alkaline earth metal ions, the transition metal ions and the ammonium ion $R^9R^{10}R^{11}R^{12}N^{\oplus}$ wherein R^9, R^{10}, R^{11} and R^{12} are independently selected from the group consisting of: hydrogen; C_1 to C_{10} alkyl;

substituted C_1 to C_{10} alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of hydroxy, halogen and C_1 to C_6 alkoxy; phenyl; benzyl; and the groups substituted phenyl and substituted benzyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio;

R^2 is selected from the group consisting of: C_1 to C_6 alkyl; C_2 to C_6 alkenyl; C_2 to C_6 haloalkenyl; C_2 to C_6 alkynyl; C_2 to C_6 haloalkynyl; substituted C_1 to C_6 alkyl wherein the alkyl group is substituted with a substituent selected from the group consisting of halogen, C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, phenyl and substituted phenyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, cyano, C_1 to C_6 alkyl, C_1 to C_6 haloalkyl, C_1 to C_6 alkoxy and C_1 to C_6 alkylthio;

R^3 is selected from the group consisting of: C_1 to C_6 alkyl, C_1 to C_6 fluoroalkyl, C_2 to C_6 alkenyl, C_2 to C_6 alkynyl and phenyl;

R^4 is selected from the group consisting of: hydrogen; halogen; cyano; C_1 to C_6 alkyl; and (C_1 to C_6 alkoxy)-carbonyl;

k is zero or the integer 1; and

n is zero or an integer selected from 1 to 4.

4. A compound according to any one of claims 1 to 3 inclusive wherein:

Z is the group -YAn wherein Y is selected from C_1 to C_6

alkyl and An is a halide anion;

X are independently selected from the group consisting of C_1 to C_6 alkyl, C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, C_1 to C_6 alkylsulfinyl, C_1 to C_6 alkylsulfonyl, halogen and C_1 to C_6 haloalkyl;

R^1 is selected from the group consisting of: hydrogen; C_2 to C_6 alkanoyl; benzoyl and substituted benzoyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, C_1 to C_6 alkyl and C_1 to C_6 alkoxy; benzenesulfonyl and substituted benzenesulfonyl wherein the benzene ring is substituted with from one to three substituents selected from the group consisting of halogen, nitro, C_1 to C_6 alkyl and C_1 to C_6 alkoxy; and an inorganic or an organic cation selected from the alkali metals, the alkaline earth metals, the transition metals, the ammonium ion and the tri- and tetra-(alkyl)-ammonium ions wherein alkyl is selected from C_1 to C_6 alkyl and C_1 to C_6 hydroxyalkyl;

R^2 is selected from the group consisting of: C_1 to C_6 alkyl, C_2 to C_6 alkenyl, C_2 to C_6 alkynyl, C_1 to C_6 haloalkyl, C_2 to C_6 haloalkenyl and C_2 to C_6 haloalkynyl;

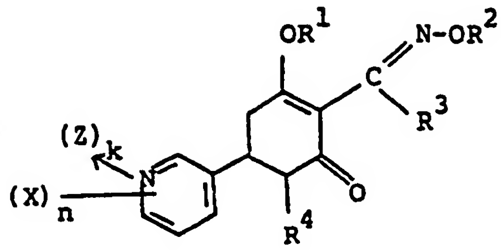
R^3 is selected from C_1 to C_6 alkyl;

R^4 is selected from hydrogen, halogen and (C_1 to C_6 alkoxy)carbonyl;

k is zero or the integer 1; and

n is zero or an integer selected from 1 to 4.

5. A compound according to any one of claims 1 to 4 inclusive of formula III



wherein:

X are independently selected from the group consisting of C_1 to C_6-alkyl, C_1 to C_6 alkoxy, halogen and C_1 to C_6 haloalkyl;

R^1 is selected from the group consisting of hydrogen, C_2 to C_6 alkanoyl, benzoyl, the alkali metals, the transition metals, the ammonium ion and the tri- and tetra-(alkyl)ammonium ions wherein alkyl is selected from C_1 to C_6 alkyl and C_1 to C_6 hydroxyalkyl;

R^2 is selected from the group consisting of: C_1 to C_3 alkyl, C_1 to C_3 haloalkyl, allyl, haloallyl and propargyl;

R^3 is selected from C_1 to C_3 alkyl;

R^4 is selected from hydrogen and (C_1 to C_6 alkoxy)-carbonyl;

k is zero; and

n is selected from the integers 3 and 4.

6. A compound according to any one of claims 1 to 5 inclusive wherein:

X are independently selected from the group consisting of C_1 to C_6 alkyl, C_1 to C_6 alkoxy, halogen and C_1 to C_6 haloalkyl;

R^1 is selected from the group consisting of hydrogen, C_2 to C_6 alkanoyl and the alkali metals;

R^2 is selected from the group consisting of C_1 to C_3 alkyl, C_1 to C_3 haloalkyl, allyl, haloallyl and propargyl;

R^3 is selected from C_1 to C_3 alkyl;

R^4 is hydrogen;

k is zero; and

n is selected from the integers 3 and 4.

7. A compound according to any one of claims 1 to 6 inclusive wherein:

X are independently selected from the group consisting of methyl, methoxy, ethoxy, bromo, chloro and trifluoromethyl;

R^1 is selected from the group consisting of hydrogen, C_2 to C_6 alkanoyl, sodium and potassium;

R^2 is selected from the group consisting of ethyl, n-propyl, allyl, propargyl, fluoroethyl and chloroallyl;

R^3 is selected from ethyl and _n_-propyl;

R^4 is hydrogen;

k is zero; and

n is an integer selected from 3 and 4.

8. A compound according to any one of claims 1 to 7 inclusive selected from the group consisting of:

2-[1-(ethoxyimino)butyl]-3-hydroxy-5-[3-(2-methoxy-4,6-dimethylpyridyl)]cyclohex-2-en-1-one;

2-[1-(ethoxyimino)butyl]-5-[3-(2-ethoxy-4,6-dimethylpyridyl)]-3-hydroxycyclohex-2-en-1-one;

2-[1-(ethoxyimino)butyl]-3-hydroxy-5-[3-(4,6-dimethyl-2-methylthiopyridyl)]cyclohex-2-en-1-one;

5-[3-(4,5-dichloro-2,6-dimethylpyridyl)]-2-[1-(ethoxyimino)butyl]-3-hydroxycyclohex-2-en-1-one;

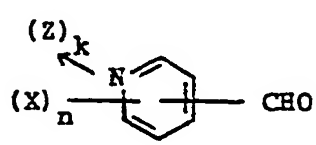
5-[3-(2,5-dichloro-4,6-dimethylpyridyl)]-2-[1-(ethoxyimino)propyl]-3-hydroxycyclohex-2-en-1-one;

5-[3-(2,5-dichloro-4,6-dimethylpyridyl)]-2-[1-(ethoxyimino)butyl]-3-hydroxycyclohex-2-en-1-one;

5-[3-(2-chloro-4,5,6-trimethylpyridyl)]-2-[1-(ethoxyimino)butyl]-3-hydroxycyclohex-2-en-1-one; and

2-[1-(ethoxyimino)butyl]-3-hydroxy-5-[3-(2-methoxy-4,5,6-trimethylpyridyl)]cyclohex-2-en-1-one.

9. A compound of formula V

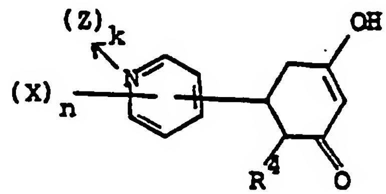


V

wherein Z, X and k are as defined according to any one of claims 1 to 7 inclusive and n is an integer selected

from 3 and 4.

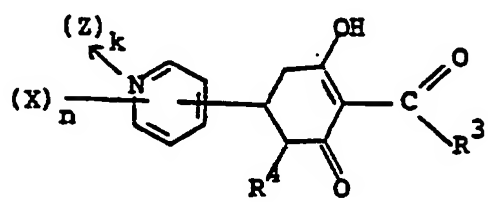
10. A compound of formula IX



IX

wherein Z, X, R^4, k and n are as defined according to any one of claims 1 to 7 inclusive.

11. A compound of formula XIII



XIII

wherein Z, X, R^3, R^4, k and n are as defined according to any one of claims 1 to 7 inclusive.

12. A herbicidal composition comprising as active ingredient a compound as defined according to any one of claims 1 to 8 inclusive and a carrier therefor.

13. A process for severely damaging or killing unwanted plants which process comprises applying to said plants, or to the growth medium of said plants, an effective amount of a compound as defined according to any one of claims 1 to 8 inclusive or an effective amount of a composition as defined according to claim 12.

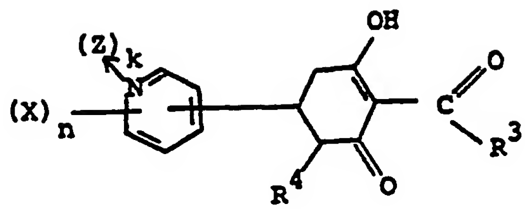
14. A process for selectively controlling the growth of monocotyledonous weeds in dicotyledonous crops which process comprises applying to said crop, or to the growth medium of said crop, a compound as defined according to any one of claims 1 to 8 inclusive or a composition as defined according to claim 12 in an amount sufficient to severely damage or kill said weeds but insufficient to substantially damage said crop.

15. A process for selectively controlling the growth of monocotyledonous weeds in cultivated crops which process comprises applying to said crop or to the growth medium of said crop a compound as defined according to any one of claims 1 to 8 inclusive or a composition as defined according to claim 12 in an amount sufficient to severely damage or kill said weeds but insufficient to substantially damage said crop.

16. A process according to any one of claims 13 to 15 inclusive wherein the compound is applied at a rate in the range of from 0.005 to 20 kilograms per hectare.

17. A process for the synthesis of a compound of formula I as defined according to any one of claims 1 to 8 inclusive which process comprises:

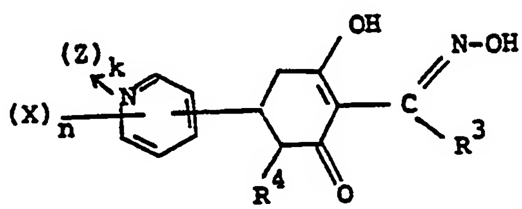
reacting 2-acyl-5-(aryl)cyclohexane-1,3-dione derivative of formula XIII with an alkoxyamine derivative of formula XVII to give a compound of the invention of formula II or reacting the 2-acyl-5-(aryl)cyclohexane-1,3-dione derivative of formula XIII with hydroxylamine and alkylating the oxime intermediate of formula XVIII with an alkylating agent of formula XIX, wherein L is a leaving group, to give a compound of the invention of formula II;



XIII

H_2NOR^2

XVII



XVIII

R^2L

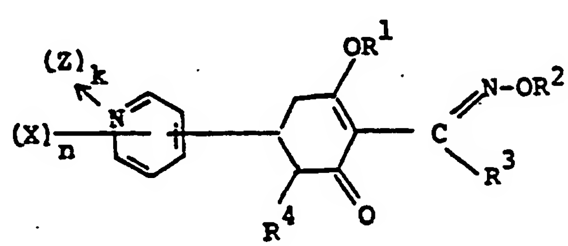
XIX

and, optionally,

reacting the compound of the invention of formula II with a compound of formula XX, wherein L is a leaving group, to give a compound of the invention of formula I.

R^1L

XX



I

18. A compound of formula I as defined according to any one of claims 1 to 8 inclusive substantially as herein described with reference to any one of Examples 1 to 12 inclusive.

19. A composition as defined according to claim 12 substantially as herein described with reference to any one of Examples 13 to 16 inclusive.

20. A process as defined according to any one of claims 13 to 16 inclusive substantially as herein described with reference to any one of Examples 14 to 16 inclusive.

21. A process as defined according to claim 17 substantially as herein described with reference to any one of Examples 1 to 12 inclusive.

DATED this day of 1983

ICI AUSTRALIA LIMITED